New Pentadentate Carboxylate-Derivatized Sulfur Ligands Affording Water Soluble Iron Complexes with [Fe(NS_4)] Cores that Bind Small Molecules (CO, NO, PMe_3) as Co-Ligands[‡]

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In the search for polydentate sulfur ligands that are able to form water-soluble iron complexes which can bind nitrogenase relevant molecules, the new pentadentate ligands py$CO_2Me$$S_4$–$H_2$ [2,6-bis[2-mercapto-3-(methoxycarbonyl)-phenylthio]dimethylpyridine] (**1**) and py$CO_2H$$S_4$–$H_2$ [2,6-bis(2-mercapto-3-carboxyphenylthio)dimethylpyridine] (**2**) having NS_4 donor atom sets and terminal thiolate donors have been synthesized. The starting material was $CO_2Me$$S_2$–$H_2$ (2,3-dimercapto benzoic acid methyl ester) which was alkylated with 2,6-bis[(tosyloxy)methyl]pyridine. The problem of specifically achieving regioselective monoalkylation of this 1,2-benzene-dithiol derivative was solved by carrying out the alkylation of $CO_2Me$$S_2$–$H_2$ at –78 °C in the presence of stoichiometric amounts of a base. Saponification of **1** afforded the carboxylic acid derivative. Coordination of py$CO_2Me$$S_4^{2-}$ to Fe^{II} in the presence of co-ligands (L = CO, PMe_3) yielded the complexes [Fe(L)(py$CO_2Me$$S_4$)] where L = CO (**5**) or PMe_3 (**4**). Upon treatment with $NOBF_4$, complex **5** afforded [Fe(NO)(py$CO_2Me$$S_4$)]$BF_4$ (**7**) which could be subsequently converted to the isolable 19 valence electron species [Fe(NO)(py$CO_2Me$$S_4$)] (**8**) upon reduction with N_2H_4. In the absence of potential co-ligands, coordination of py$CO_2Me$$S_4^{2-}$ to Fe^{II} afforded the dinuclear complex [Fe(py$CO_2Me$$S_4$)]$_2$ (**6**) whilst coordination to Ni^{II} gave [Ni(py$CO_2Me$$S_4$)]$_x$ (**3**). Solubility of these complexes in water could be achieved by replacing the CO_2Me groups with CO_2H substituents. The ligand py$CO_2H$$S_4^{2-}$ afforded the iron complexes [Fe(L)(py$CO_2H$$S_4$)] [L = CO (**10**) and PMe_3 (**12**)] and [Fe(NO)(py$CO_2H$$S_4$)]$BF_4$ (**11**). Both **10** and **12** could be reversibly deprotonated to give the corresponding water-soluble salts $(NMe_4)_2$[Fe(L)(*py*$CO_2$$S_4$)] with L = CO {$(NMe_4)_2$ [**9**]} and PMe_3 {$(NMe_4)_2$ [**13**]}. The complexes were characterized by elemental analysis, spectroscopic methods and X-ray structural determinations. The molecular structure of [Fe(PMe_3)(py$CO_2H$$S_4$)] (**12**) was found to exhibit inter- and intramolecular O–H···O and O–H···S hydrogen bonds which serve as models for proton transfer steps from external sources to the active sites of metal sulfur enzymes.

Introduction

Iron atoms in sulfur dominated coordination spheres constitute the active sites of numerous metal enzymes.[1] In the search for low-molecular weight complexes which are capable of modeling characteristic features of the active sites of FeMo, FeV or FeFe nitrogenases such as the sulfur environment of the iron centers, binding of small molecules, and redox-activity, we have recently discovered the [Fe(pyS_4)] fragment (see Figure 1).[2]

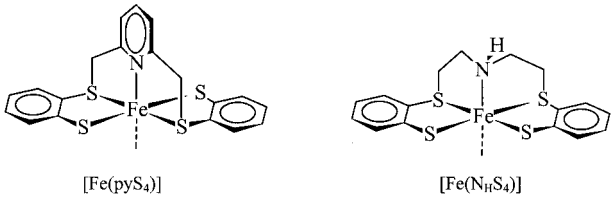

Figure 1. Schematic structure of [Fe(pyS_4)] and [Fe(N_HS_4)] fragments

This fragment binds small molecules, e.g. CO, N_2H_2, N_2H_4, NH_3.[3] The resultant complexes are redox-active and are formed diastereoselectively, always exhibiting the thiolate and thioether donors in *trans* positions. In contrast with related [Fe(L)(N_HS_4)][4] complexes of the pentadentate ligand $N_HS_4^{2-}$ [= dianion of 2,2′-bis(2-mercapto-phenylthio)diethylamine] which may contain low- or high-spin Fe^{II} depending on the σ or σ-π character of the ligand L, all 18 valence electron [Fe(L)(pyS_4)] complexes are diamagnetic. This was demonstrated, for example, by [Fe(CO)-

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(pyS_4)] and [Fe(N_2H_4)(pyS_4)] which are both diamagnetic.[3] [Fe(L)(pyS_4)] complexes are, however, usually soluble only in non-aqueous solvents thus preventing any investigations in water which is clearly the important solvent in biological systems. In order to resolve this problem and to obtain water-soluble complexes, we attempted to introduce carboxylic acid substituents into the pyS_4^{2-} ligand. This required new ligands, the design and synthesis of which are reported here together with some related iron and nickel complexes.

Results and Discussion

Ligand Synthesis

Figure 2 summarizes starting materials, notations and the target ligands **1** and **2**.

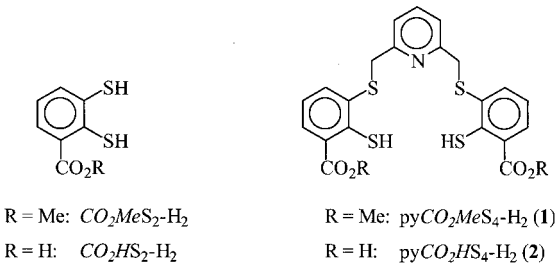


Figure 2. Starting materials, notations and the target ligands **1** and **2**

The notations $CO_2MeS_2{-}H_2$, $pyCO_2MeS_4{-}H_2$, $pyCO_2HS_4{-}H_2$, etc. have been used throughout in order to facilitate legibility and designation of the degrees of protonation/deprotonation of the individual ligands.

The starting material for the pentadentate target ligand **1** was $CO_2MeS_2{-}H_2$, and the major problem was to connect two of these molecules with 2,6-bis[(tosyloxy)methyl]-pyridine such that only one of the two SH functions in $CO_2MeS_2{-}H_2$ would be regioselectively alkylated.

All attempts to achieve a regioselective mono-alkylation using [$Fe^{II}(CO)_2$] or [Ni^{II}] complex fragments as templates remained unsuccessful, although such template reactions have afforded very good results in previous preparations of related ligands.[5] Analogous attempts with the acid derivative $CO_2HS_2{-}H_2$ also failed, as did direct alkylations of $CO_2MeS_2{-}H_2$ under ambient conditions in the absence of templates. In all cases an inseparable mixture of the three regioisomers **1**, **1a**, and **1b** was obtained (Figure 3).

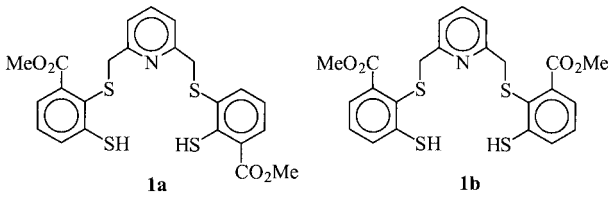
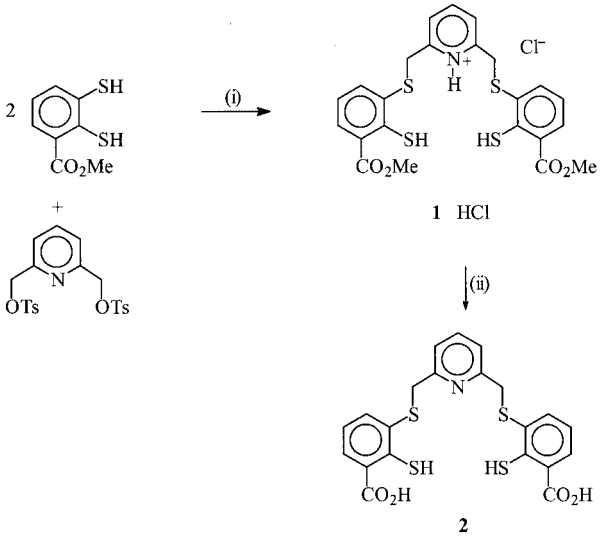


Figure 3. Isomers of $pyCO_2MeS_4{-}H_2$ (**1**)

After a number of laborious experiments, it was finally found that alkylation of $CO_2MeS_2{-}H_2$ in the presence of one equivalent of NMe_4OH at −78 °C afforded the target molecule **1** as the major product. Even then however, a purification step via the nickel complex [Ni($pyCO_2MeS_4$)]$_x$ was necessary. Acidic hydrolysis of [Ni($pyCO_2MeS_4$)]$_x$ afforded **1** as its HCl salt in isomeric purity after recrystallization. Saponification of the ester functions of **1** gave the acid derivative $pyCO_2HS_4{-}H_2$ (**2**) (Scheme 1).



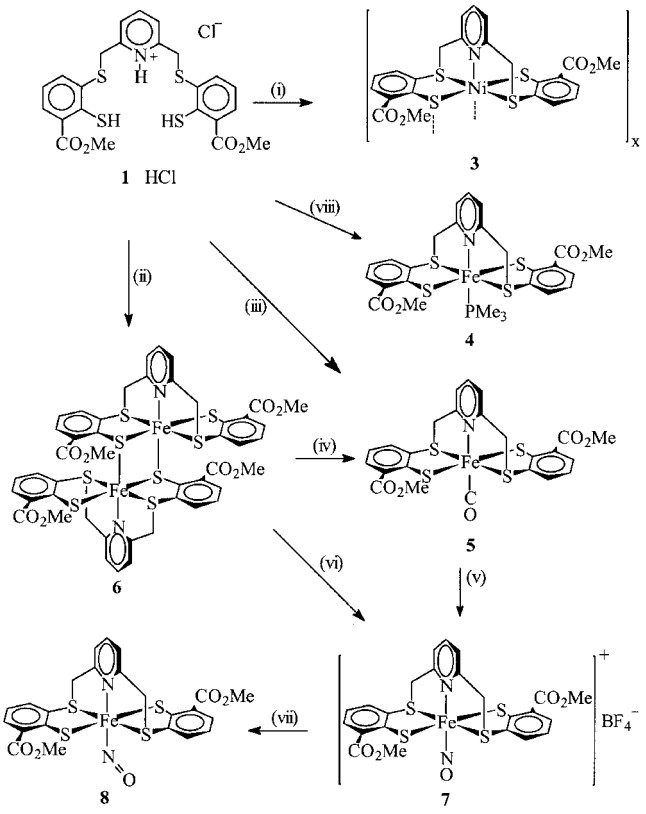
Scheme 1. Synthesis of the target ligands **1** and **2**: (i) 1) +2 NMe_4OH, −78 °C, THF/MeOH, 15 h; 2) $HCl_{aq.}$, CH_2Cl_2; 3) +2 LiOMe, + $Ni(OAc)_2{\cdot}4H_2O$, MeOH; 4) $HCl_{aq.}$, CH_2Cl_2. (ii) 1) +10 $NaOH_{aq.}$, THF, 72 h; 2) $HCl_{aq.}$, CH_2Cl_2

Neither ^1H nor ^{13}C NMR spectroscopy enabled us to unambiguous distinguish the target ligand **1** from its symmetrical regioisomer **1b**. This was possible only by an X-ray structural determination (vide infra).

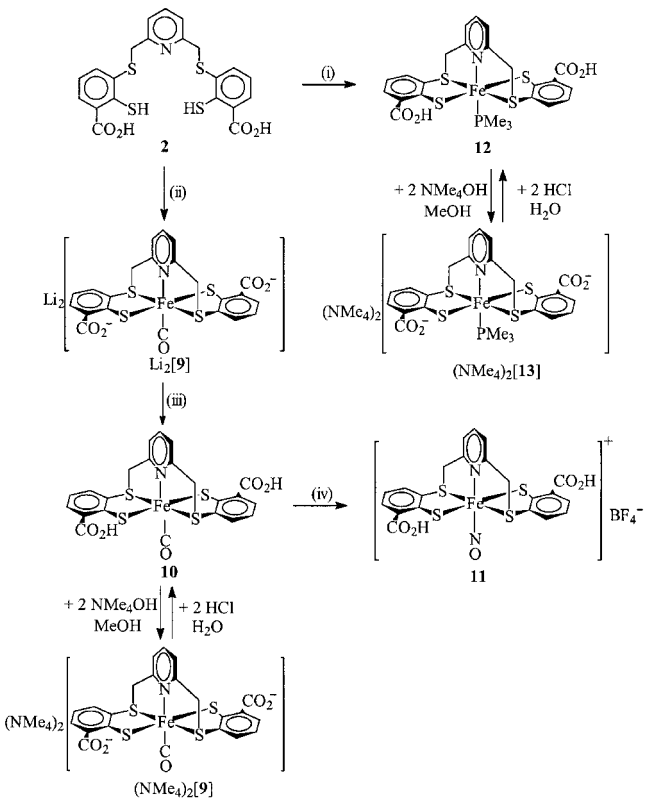
Syntheses of Iron and Nickel Complexes

Straightforward coordination of the anion $pyCO_2MeS_4^{2-}$ to Fe^{II} and Ni^{II} afforded a series of complexes which are shown in Scheme 2.

Reaction of **1**·HCl with $Ni(OAc)_2{\cdot}4H_2O$ in the presence of three equivalents of LiOMe (for deprotonation of the pyridinium NH and thiol SH functions) afforded yellow-brown [Ni($pyCO_2MeS_4$)]$_x$ (**3**) which is presumably dinuclear like the analogous [Ni(pyS_4)]$_2$.[2] Complex **3** is moderately soluble in DMF and DMSO but only sparingly soluble in all other common solvents. Analogous reactions of **1**·HCl with $FeCl_2{\cdot}4H_2O$ in the presence of PMe_3 or CO gave red [Fe(PMe_3)($pyCO_2MeS_4$)] (**4**) and red [Fe(CO)($pyCO_2MeS_4$)] (**5**), respectively, with **5** showing a ν(CO) band at 1952 cm^{-1} in KBr. In the absence of potential co-ligands, dinuclear violet-red [Fe($pyCO_2MeS_4$)]$_2$ (**6**) was formed instead. Complex **6** is almost insoluble in all common solvents although THF suspensions of **6** react with gaseous CO to give **5** indicating that **6** partially dissociates into coordinatively unsaturated [Fe($pyCO_2MeS_4$)] monomers. Treatment of the carbonyl complex [Fe(CO)($pyCO_2MeS_4$)]



Scheme 2. Fe and Ni complexes with [M(pyCO_2MeS$_4$)] fragments: (i) +3 LiOMe, + $Ni(OAc)_2{\cdot}4H_2O$, MeOH; (ii) +3 LiOMe, + $FeCl_2{\cdot}4H_2O$, MeOH; (iii) +3 LiOMe, + $FeCl_2{\cdot}4H_2O$, + exc. CO, MeOH; (iv) + exc. CO, THF; (v) + $NOBF_4$, CH_2Cl_2; (vi) +2 $NOBF_4$, CH_2Cl_2; (vii) + exc. H_2N_4, MeOH; (viii) +3 LiOMe, + $FeCl_2{\cdot}4H_2O$, + exc. PMe_3, MeOH



Scheme 3. Synthesis of acidic [Fe(L)(pyCO_2HS$_4$)] complexes and corresponding salts with [Fe(L)(pyCO_2S$_4$)]$^{2-}$ anions: (i) + $FeCl_2{\cdot}4H_2O$, + exc. PMe_3, MeOH; (ii) +4 LiOMe, + $FeCl_2{\cdot}4H_2O$, + exc. CO, MeOH; (iii) +2 HCl, H_2O (iv) + $NOBF_4$, CH_2Cl_2

(**5**) with $NOBF_4$ led to CO substitution and formation of the brown 18 valence electron nitrosyl derivative [Fe(NO)(pyCO_2MeS$_4$)]BF_4 (**7**) having a ν(NO) band at 1881 cm^{-1}. Complex **7** also formed when dinuclear **6** was treated with an excess of $NOBF_4$. Reduction of **7** with hydrazine gave the neutral red-brown [Fe(NO)(pyCO_2MeS$_4$)] (**8**) having a ν(NO) band at 1617 cm^{-1}.

Preparation of complexes with the acid derivative pyCO_2HS$_4$−H_2 (**2**) or its fully deprotonated anion pyCO_2S$_4^{4-}$ were generally achieved in the same way (Scheme 3). The resultant complexes enabled studies of the reversible deprotonations and the electronic influence of carboxylic acid vs. carboxylate functions. It proved difficult to obtain analytically pure samples of salts containing [Fe(pyCO_2S$_4$)]$^{2-}$ anions. Recrystallization attempts of these salts always afforded powders and, in fact, single crystals suitable for an X-ray diffraction study could not be obtained.

Reaction of pyCO_2HS$_4$−H_2 (**2**) with four equivalents of LiOMe and subsequent treatment with $FeCl_2{\cdot}4H_2O$ and CO afforded Li_2[Fe(pyCO_2S$_4$)] (Li_2[**9**]). This compound tenaciously retained varying amounts of LiCl, H_2O, and MeOH. Its identity, however, was confirmed by IR and NMR spectroscopy and by its reaction with aqueous HCl which afforded the neutral complex [Fe(CO)(pyCO_2HS$_4$)] (**10**). Complex **10** could be reversibly deprotonated with NMe_4OH to give $(NMe_4)_2$[Fe(CO)(pyCO_2S$_4$)] {$(NMe_4)_2$[**9**]} and treatment of **10** with $NOBF_4$ afforded the corresponding nitrosyl complex [Fe(NO)(pyCO_2HS$_4$)](BF_4) (**11**) (ν(NO): 1900 cm^{-1} in KBr). Complex **11** could not be isolated in an analytically pure form but its identity was established from a combination of NMR and IR spectroscopy. Surprisingly, the PMe_3 complex [Fe(PMe_3)(pyCO_2HS$_4$)] (**12**) formed directly from neutral pyCO_2HS$_4$−H_2 and $FeCl_2{\cdot}4H_2O$ in the presence of an excess of PMe_3. The excess PMe_3 presumably acts as base giving PMe_3H^+ cations which result in the appropriate proton concentration needed for formation of neutral **12**. Deprotonation of **12** with NMe_4OH gave the salt $(NMe_4)_2$[Fe(PMe_3)(pyCO_2S$_4$)] {$(NMe_4)_2$[**13**]}.

X-ray Structural Determinations

X-ray structural determinations were indispensable for confirming the regioselectivity of the alkylation reactions (vide supra). Figure 4 shows the molecular structures of pyCO_2MeS$_4$−H_2·HCl (**1**·HCl), [Fe(CO)(pyCO_2MeS$_4$)] (**5**), [Fe(pyCO_2MeS$_4$)]$_2{\cdot}H_2O{\cdot}$THF (**6**·H_2O·THF) and [Fe(PMe_3)(pyCO_2HS$_4$)]·0.25MeOH (**12**·0.25MeOH). Table 1 lists selected distances and angles.

The ligand **1**·HCl exhibits C_2 symmetry in the solid state. The carboxylic acid methyl ester substituents are located in positions *ortho* to the thiol functions. The Cl^- counterion

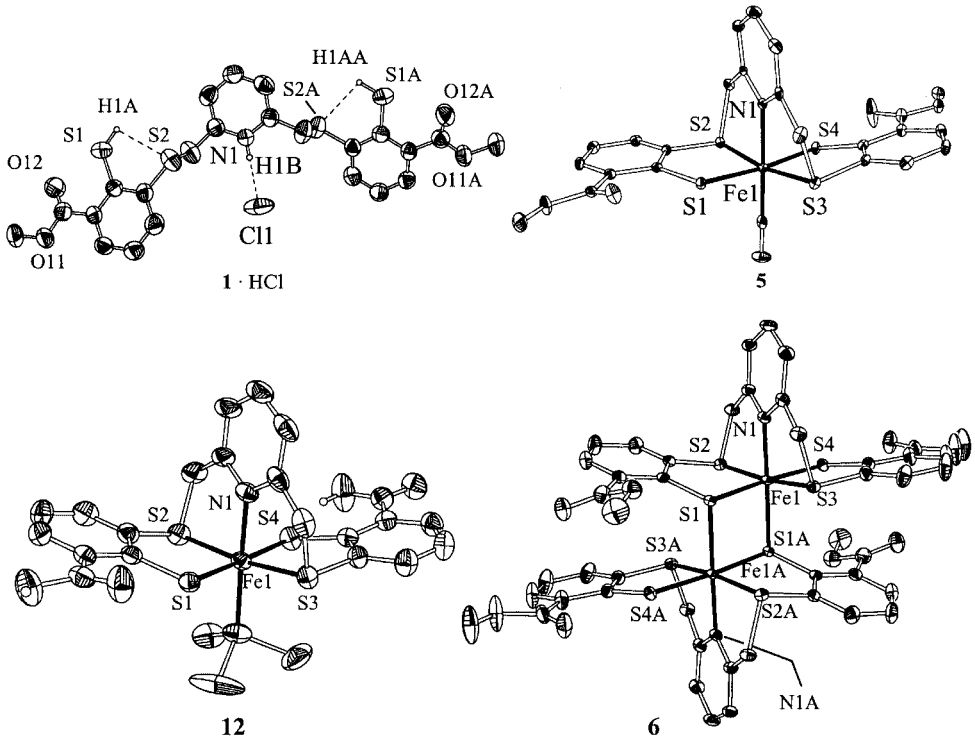


Figure 4. Molecular structures of pyCO_2MeS$_4$−H$_2$·HCl (**1**·HCl), [Fe(CO)(pyCO_2MeS$_4$)] (**5**), [Fe(pyCO_2MeS$_4$)]$_2$·H$_2$O·THF (**6**·H$_2$O·THF) and [Fe(PMe$_3$)(pyCO_2HS$_4$)]·0.25MeOH (**12**·0.25MeOH) (50% probability ellipsoids, C-bonded H atoms and solvent molecules omitted)

Table 1. Selected distances (pm) and angles (deg) of [Fe(CO)(pyCO_2MeS$_4$)] (**5**), [Fe(pyCO_2MeS$_4$)]$_2$·H$_2$O·THF (**6**·H$_2$O·THF) and [Fe(PMe$_3$)(pyCO_2HS$_4$)]·0.25MeOH (**12**·0.25MeOH)

Complex	**5**	**6**	**12**
Fe1−N1	201.0(2)	197.8(3)	200.4(3)
Fe1−S1	230.79(6)	227.7(1)	229.5(1)
Fe1−S2	220.05(6)	222.1(1)	220.9(1)
Fe1−S3	221.80(6)	220.9(1)	220.4(1)
Fe1−S4	228.41(6)	228.7(1)	227.7(1)
Fe1−L	174.1(2)	234.8(1)	223.4(1)
N1−Fe1−S3	84.83(5)	86.29(9)	85.02(8)
N1−Fe1−S4	90.12(6)	88.03(9)	89.84(7)
S1−Fe1−S4	174.19(2)	176.12(4)	176.53(4)
S2−Fe1−S4	85.35(2)	93.84(4)	88.95(3)
S2−Fe1−S1	89.75(2)	88.61(4)	89.03(3)
S3−Fe1−S4	90.05(2)	89.51(4)	88.89(3)
S2−Fe1−S3	169.86(2)	170.40(4)	170.05(4)

forms a hydrogen bond to the protonated pyridine N atom.

The metal centers of all the complexes are six-coordinate and exhibit pseudo octahedral geometries. The thiolate and thioether donors always adopt *trans* positions to each other with the pyridine N donors in apical positions such that square pyramidal [MNS$_4$] cores result. This indicates that the rigid bis-methylene-pyridine bridge connecting the 1,2-benzene-dithiol fragments exerts a stereochemical directing influence. The sixth positions of the pseudo-octahedral metal centers are occupied either by the co-ligand L (CO, PMe$_3$) or a thiolate donor of another [MNS$_4$] core. Dinuclear [Fe(pyCO_2MeS$_4$)]$_2$ possesses a crystallographically imposed inversion center and contains both enantiomers of the chiral [Fe(pyCO_2MeS$_4$)] fragment. **5** crystallizes in the chiral space group $P2_1$ and contains only one enantiomer.

Distances and angles show no anomalies and lie in the range observed for the parent complex [Fe(CO)(pyS$_4$)].[2] The Fe−N(pyridine) distances range from 197. 8(3) to 201.2(6) pm in **6** and **7** respectively. Fe−S(thioether) distances (≈221 pm) are always shorter than Fe−S(thiolate) distances (≈228 pm) within the [FeNS$_4$] cores. The Fe−S distances to the bridging thiolate donors in dinuclear **6** are distinctly longer (≈234 pm) indicating the tendency of **6** to dissociate into mononuclear [Fe(pyCO_2MeS$_4$)] fragments.

The structure of [Fe(PMe$_3$)(pyCO_2HS$_4$)] (**12**) deserves special interest because the crystal lattice contains chains of [Fe(PMe$_3$)(pyCO_2HS$_4$)] molecules which are connected by intermolecular O−H···O hydrogen bonds. Each [Fe(PMe$_3$)-(pyCO_2HS$_4$)] molecule exhibits an additional intramolecular O−H···S(thiolate) hydrogen bond. Figure 5 shows part

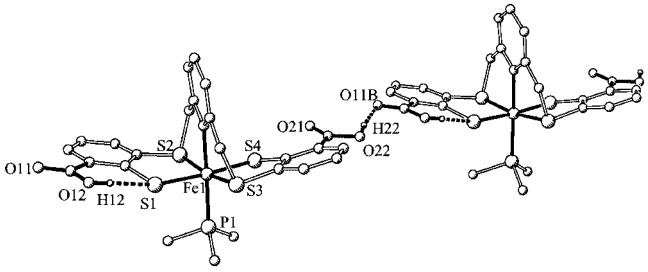


Figure 5. Intra- and intermolecular hydrogen bonds of [Fe(PMe$_3$)-(pyCO_2HS$_4$)] (**12**)

of the crystal lattice consisting of chains that each contain only homochiral molecules.

The presence of intermolecular hydrogen bonds can be inferred from the distances *d*(O22−H22) = 82 pm, *d*(H22···O11B) = 193 pm, *d*(O22···O11b) = 274.1(4) pm and the angle [O22−H22···O11B] = 170.8°. The intramolecular O−H···S hydrogen bonds are indicated by the distances *d*(O12−H12) = 82 pm, *d*(H12···S1) = 211 pm, *d*(O12···S1) = 289.0(3) pm and the angle [O12−H12···S1] = 159.4°. In particular, the *d*(H12···S1) distance is considerably shorter than the sum of van der Waals radii of sulfur and hydrogen (r_H = 100 pm, r_S = 180 pm)[7] and suggests a strong S···H interaction. Such a strong S···H interaction is also indicated by an IR band in **12** at 2612 cm^{-1} (in KBr). This band can be assigned to a ν(OH) vibration strongly lowered in energy by hydrogen-bonding or alternatively to a ν(SH) vibration indicating protonation of the thiolate donor. The two types of hydrogen bonds in which the carboxylic acid groups are involved make these groups vibrationally inequivalent such that two different $\nu(CO)_{COOH}$ bands can be observed in the IR (KBr) spectrum of **12** at 1701 and 1668 cm^{-1}.

Inter- and intramolecular hydrogen bonds like those observed in **12** are of interest because they can serve as models for the transport of protons in metal sulfur enzyme proteins. Protons from an external source first bind to carboxylic acid/carboxylate side chains of the protein, migrate from there to Brønsted-basic sulfur sites and, if needed in an [H^+/e^-] coupled enzyme reaction, to a substrate molecule coordinated to a metal center.

General Properties and Spectroscopic Characterization of Complexes

A major goal of this work was to achieve water solubility of specific complexes by the rational design of ligands. This objective was successfully accomplished with lithium and ammonium salts of the anions $[Fe(CO)(py\mathit{CO_2}S_4)]^{2-}$ (**9**) and $[Fe(PMe_3)(py\mathit{CO_2}S_4)]^{2-}$ (**13**). The salts Li_2[**9**], $(NMe_4)_2$[**9**], and $(NMe_4)_2$[**13**] are soluble in H_2O and water-like solvents such as MeOH. All the other complexes are sparingly soluble or insoluble in H_2O or MeOH. The low solubility of neutral $[Fe(CO)(py\mathit{CO_2H}S_4)]$ (**5**) or $[Fe(PMe_3)(py\mathit{CO_2H}S_4)]$ (**12**) in H_2O corresponds to the insolubility in water of higher aliphatic or aromatic carboxylic acids.

All complexes were characterized by elemental analysis and common spectroscopic methods. The IR (KBr) spectra of the CO complexes exhibit characteristic ν(CO) bands in the region 1970−1949 cm^{-1} and those of the 18 VE nitrosyl complexes $[Fe(NO)(py\mathit{CO_2R}S_4)](BF_4)$ [R = Me (**7**), R = H (**11**)] display ν(NO) bands at 1881 and 1900 cm^{-1}. The ν(NO) band of the neutral 19 valence electron species appears at 1617 cm^{-1}, indicating that the unpaired electron occupies an antibonding orbital. As shown by DFT calculations for the related parent complex $[Fe(NO)(pyS_4)]$, this molecular orbital is antibonding with respect to all Fe−ligand interactions and has a large contribution from a π* type NO orbital.[8]

^{1}H NMR spectroscopy proved to be particularly suitable for quickly checking the purity and symmetry of the ligands and complexes. The ^{1}H and ^{13}C NMR spectra show typical signals for pyS_4 cores corroborating the two-fold symmetry for all compounds. Like $[Fe(PR_3)(pyS_4)]$ (R = PMe_3, $PnPr_3$), the PMe_3 complexes **4**, **12**, and $(NMe_4)_2$[**13**] show sharp ^{1}H NMR signals only in the presence of an excess of PMe_3. This has been previously explained by suggesting the occurrence of a reversible dissociation of the phosphane ligands in solution.[3]

Electronic Influence of Benzene Ring Substituents

CO_2R (R = alkyl, H) substituents are generally considered to withdraw electron density from benzene rings by inductive or mesomeric effects. It was therefore of interest to examine whether such an electron-withdrawing effect of the CO_2R substituents would reach beyond the thioether and thiolate donors and be detectable at the metal centers of the homologous complexes. This question was probed by examining the ν(CO) frequencies of the iron complexes listed in Table 2.

Table 2. ν(CO) Frequencies of iron carbonyl complexes with $[Fe(pyS_4)]$ cores [cm^{-1}]

Complex	In KBr	In solution
$[Fe(CO)(pyS_4)]$	1963	1974 (THF)[9]
$[Fe(CO)(pyS_4)]\cdot MeOH$	1955[2]	–
$[Fe(CO)(py\mathit{CO_2Me}S_4)]$	1952	1974 (THF)
$[Fe(CO)(py\mathit{CO_2H}S_4)]$	1962	1963 (DMF)
$Li_2[Fe(CO)(py\mathit{CO_2}S_4)]\cdot H_2O\cdot 3MeOH\cdot LiCl$	1969	1973 (MeOH)
$(NMe_4)_2[Fe(CO)(py\mathit{CO_2}S_4)]\cdot 2H_2O$	1949	1973 (MeOH)
$[Fe(CO)(py^{\mathit{bu}}S_4)]$	1969	1969 (THF)[9]

Table 2 demonstrates that all CO complexes show very similar or almost identical ν(CO) frequencies in solution indicating that different benzene ring substituents have practically no influence upon the electron density at the iron centers. In the solid state (KBr), the ν(CO) frequencies, although lying in the same range, show larger differences. As evidenced by both $[Fe(CO)(pyS_4)]$[9] and $[Fe(CO)(pyS_4)]\cdot MeOH$,[2] however, the presence of a lattice MeOH molecule can cause a wavenumber shift of 8 cm^{-1}. Conversely, $[Fe(CO)(py\mathit{CO_2H}S_4)]$ and $[Fe(CO)(py^{\mathit{bu}}S_4)]$[9] show practically identical ν(CO) frequencies in KBr, although two electron-withdrawing CO_2H substituents have been replaced by four electron donating tertiary butyl substituents. In conclusion, the results indicate that the benzene ring substituents have no significant influence upon the electron density at the metal center but, rather, the ν(CO) shifts observed are due to solvation or crystal packing effects. This conclusion is supported by cyclic voltammetry (CV) studies. The isoelectronic iron carbonyl complexes $[Fe(CO)(pyS_4)]$,[9] $[Fe(CO)(py\mathit{CO_2Me}S_4)]$, and $[Fe(CO)(py\mathit{CO_2H}S_4)]$ each show a reversible redox wave in the anodic region.

Table 3 lists the redox potentials of the three complexes in either CH_2Cl_2 or DMF.

Table 3. Redox potentials of carbonyl complexes with [Fe(pyS_4)] cores [mV]

Complex	CH_2Cl_2	DMF
[Fe(CO)(pyS_4)]	460	468
[Fe(CO)(pyCO_2MeS_4)]	514	539
[Fe(CO)(pyCO_2HS_4)]	–	490

The potentials (Table 3) indicate that CO_2R substituents render complexes with [Fe(pyS_4)] cores more difficult to oxidize. Conversely, when changing from CO_2Me to CO_2H, the trend in redox potentials is reversed. In addition the overall shifts of the redox potentials in the range of 22−71 mV (in DMF) are small. Taking into account also the fact that redox potentials in solution are sensitive towards the nature of the solvent and solvation effects (cf. the values in CH_2Cl_2 and DMF), it can safely be assumed that the ν(CO) frequencies listed in Table 2 indeed confirm that CO_2R substituents do not have a significant influence upon the electron density at the metal centers or [Fe(L)(NS_4)] cores.

Concluding Discussion

Two new pentadentate ligands containing NS_4 donor atom sets and terminal thiolate donors have been synthesized and coordinated to Fe^{II} and Ni^{II} centers affording a series of new iron and nickel complexes. The general problem of achieving a regioselective and specific mono-alkylation of the nearly equivalent thiol functions in the 1,2-benzenedithiol derivative $CO_2MeS_2-H_2$ could be solved by carrying out the alkylation at low temperature in the presence of limited amounts of a base (1 NMe_4OH:1 $CO_2MeS_2-H_2$) affording the target ligand py$CO_2MeS_4-H_2$ (**1**). Saponification of py$CO_2MeS_4-H_2$ (**1**) gave the acid derivative py$CO_2HS_4-H_2$ (**2**) that enabled synthesis of [Fe(L)(pyCO_2HS_4)] complexes (L = CO, PMe_3). These complexes become water-soluble upon deprotonation of the CO_2H substituents and form salts of the type (cation)$_2$[Fe(L)(pyCO_2S_4)] which had been the primary goal of this work.

Spectroscopic, electrochemical and X-ray structural results indicate that introducing CO_2Me or CO_2H substituents into the benzene rings of [Fe(L)(pyS_4)] complexes does not change the electron density at the Fe centers significantly. This is important for further investigations since achieving water solubility of the [Fe(L)(pyS_4)] complexes was the major goal but without changing the coordination properties of the iron centers that bind a considerable number of small molecules relevant to nitrogenase.

The X-ray structure of [Fe(PMe_3)(pyCO_2HS_4)] (**12**) further revealed that such complexes can form inter- and intramolecular O−H···O and O−H···S(thiolate) bonds. These hydrogen bonds may serve as models for the transport of protons from external sources to the metal centers of enzymes when small molecules binding to these centers are reduced by coupled [H^+/e^-] transfer steps.

Experimental Section

General Methods: Unless noted otherwise, all procedures were carried out under nitrogen using standard Schlenk techniques at room temperature with stirring. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated): Perkin−Elmer 16PC FTIR. NMR: Jeol-JNM-GX 270, JNM-EX 270 and JNM-LA 400 with the residual signals of the deuterated solvent used as an internal reference. Spectra were recorded at 25 °C. Mass spectra: JEOL MSTATION 700 spectrometer. Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. Magnetic susceptibility: Johnson Matthey susceptibility balance. Cyclic voltammetry was performed with a Radiometer Copenhagen IMT 102 electrochemical interface using a three-electrode cell with a glassy carbon (Radiometer Copenhagen EDI) working electrode and Pt reference and counter electrodes. Solutions were 10^{-3} M; $NBu_4[PF_6]$ (10^{-1} M) was used as the supporting electrolyte. Potentials were referenced to the normal hydrogen electrode (NHE) using Fc/Fc^+ as an internal standard (E_{Fc/Fc^+} = 0.4 V vs. NHE).[11] "S_2"-H_2 (1,2-benzene-dithiol),[12] $CO_2MeS_2-H_2$ (2,3-dimercapto benzoic acid methyl ester),[13] and 2,6-bis[(tosyloxy)methyl]pyridine[14] were prepared as described in the literature.

py$CO_2MeS_4-H_2$ (1): A yellow solution of $CO_2MeS_2-H_2$ (17.38 mmol, 3.48 g) and NMe_4OH (17.38 mmol, 7.36 mL of a 25% solution in MeOH) in THF (100 mL) was combined with a solution of 2,6-bis[(tosyloxy)methyl]pyridine (3.89 g, 8.69 mmol) in THF (130 mL) at −78 °C. After 2 h at −78 °C and 15 h at room temperature the resultant white precipitate was separated by filtration and washed with THF (35 mL). The combined filtrates were evaporated and the remaining residue was dissolved in CH_2Cl_2 (100 mL). Concentrated hydrochloric acid (20 mL) was added and the resultant mixture was stirred vigorously for 5 min. The CH_2Cl_2 phase was separated from the aqueous phase, washed with water (5 × 25 mL) until a pH of 7 was attained, dried over Na_2SO_4 and the solvents evaporated. The resultant almost colorless solid foam was suspended in MeOH (75 mL), and LiOMe (17.33 mmol, 17.33 mL of a 1 M solution in MeOH) was added. The resultant solution was filtered and combined with a solution of $Ni(OAc)_2{\cdot}4H_2O$ (2.16 g, 8.68 mmol) in MeOH (40 mL). The yellow-brown precipitate thus obtained was separated by filtration after 1 h, washed with MeOH (30 mL), dried in vacuo and suspended in CH_2Cl_2 (120 mL). Concentrated hydrochloric acid (30 mL) was added and the mixture was stirred vigorously for 20 min. The CH_2Cl_2 phase was separated from the acidic green aqueous phase, dried over Na_2SO_4 and the solvents evaporated. The resultant yellow solid foam was recrystallized from CH_2Cl_2/*n*-hexane to give green-yellow crystals. Yield: 2.33 g py$CO_2MeS_4-H_2{\cdot}$HCl (**1**·HCl) (61%).^{1}H NMR ($CDCl_3$, 269.60 MHz): δ = 18.2 (br., 2 H, N*H*), 7.97 (vdd, 2 H, C_6H_3), 7.80 (vt, 1 H, H_γ, pyridine), 7.59 (vdd, 2 H, C_6H_3), 7.17 (vd, 2 H, H_β, pyridine), 7.06 (vt, 2 H, C_6H_3), 6.58 (s, 2 H, S*H*), 4.65 (s, 4 H, CH_2), 3.87 (s, 6 H, CO_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.83 MHz): δ = 167.3 (CO_2CH_3), 154.2, 143.6, 139.4, 132.4, 132.3, 131.7, 127.2, 124.3 [*C*(aryl)], 52.6 (CO_2CH_3), 36.3 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2486 (br. m, N−H + S−H), 1714 cm^{-1} (s, C=O). MS (FD^+, CH_2Cl_2): *m*/*z* = 504 [py$CO_2MeS_4-H_3]^+$.

$C_{23}H_{22}ClNO_4S_4$ (540.14): calcd. C 51.14, H 4.11, N 2.59, S 23.75; found C 51.36, H 4.10, N 2.61, S 23.62.

pyCO_2HS$_4$−H$_2$ (2): A suspension of **1**·HCl (1.00 g, 1.85 mmol) and NaOH (18.5 mmol, 18.5 mL of a 1 M solution in H_2O) in THF (20 mL) was stirred vigorously for 24 h, reduced to one half of its volume, stirred again for 48 h and then filtered. Concentrated hydrochloric acid (18.5 mmol, 18.5 mL) was added to the pale yellow filtrate. The resultant pale yellow precipitate was separated by filtration, washed with H_2O (60 mL) and dried in vacuo. Yield: 0.815 g pyCO_2HS$_4$−H$_2$ (**2**) (93%). ^{1}H NMR ([D$_8$]1,4-dioxane, 269.72 MHz): δ = 11.73 (br., 2 H, CO_2H), 7.95 (vdd, 2 H, C_6H_3), 7.54 (vdd, 2 H, C_6H_3), 7.50 (vt, 1 H, H_γ, pyridine), 7.13 (br., 2 H, S*H*), 7.07 (vd, 2 H, H_β, pyridine), 7.00 (vt, 2 H, C_6H_3), 4.23 (s, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR ([D$_8$]1,4-dioxane, 67.83 MHz): δ = 169.2 (*C*OOH), 157.8, 143.4, 138.3, 137.6, 135.5, 132.1, 127.6, 124.3, 122.5 [C(aryl)], 40.6 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (br. m, O−H), 2490 (m, S−H), 1685 cm^{-1} (s, C=O). MS (FD$^+$; 1,4-dioxane): *m*/*z* = 476 [pyCO_2HS$_4$−H$_2$]$^+$. $C_{21}H_{17}NO_4S_4$ (475.63): calcd. C 53.03, H 3.60, N 2.94, S 26.97; found C 52.98, H 3.47, N 3.01, S 26.85.

[Ni(pyCO_2MeS$_4$)]$_x$ (3): To a suspension of **1**·HCl (0.400 g, 0.74 mmol) in MeOH (30 mL) and THF (10 mL) was added LiOMe (2.22 mmol, 2.22 mL of a 1 M solution in MeOH). The resultant yellow solution was filtered, and a solution of Ni(OAc)$_2$·4 H_2O (0.160 g, 0.64 mmol) in MeOH (12 mL) was added dropwise. The yellow-brown precipitate which formed was separated by filtration, washed with MeOH and dried in vacuo. Yield: 0.288 g [Ni(pyCO_2MeS$_4$)]$_x$ (**3**) (80%). IR (KBr): $\tilde{\nu}$ = 1721 cm^{-1} (s, C=O). MS (FD, DMF): *m*/*z* = 559 [Ni(pyCO_2MeS$_4$)]$^+$. $C_{23}H_{19}NNiO_4S_4$ (560.36): calcd. C 49.30, H 3.42, N 2.50, S 22.89; found C 49.39, H 3.42, N 2.29, S 22.64.

[Fe(PMe$_3$)(pyCO_2MeS$_4$)] (4): A solution of $FeCl_2$·4 H_2O (0.073 g, 0.37 mmol) in MeOH (8 mL) was added to a solution of **1**·HCl (0.199 g, 0.37 mmol), LiOMe (1.1 mmol, 1.1 mL of a 1 M solution in MeOH) and PMe_3 (0.073 mL, 0.74 mmol) in MeOH (25 mL). After 2 h the resultant red precipitate was separated by filtration, washed with MeOH (15 mL) and Et_2O (15 mL), and dried in vacuo. Yield: 0.170 g [Fe(PMe$_3$)(pyCO_2MeS$_4$)] (**9**) (73%). ^{1}H NMR (CD_2Cl_2, exc. PMe_3, 399.65 MHz): δ = 7.65 (vdd, 2 H, C_6H_3), 7.31 (vdd, 2 H, C_6H_3), 7.05 vt, 1 H, H_γ, pyridine), 6.92 (vd, 2 H, H_β, pyridine), 6.71 (vt, 2 H, C_6H_3), 4.70 (d, 2 H, CH*H*), 4.35 (d, 2 H, C*H*H), 3.63 (s, 6 H, CO_2CH_3), 0.96 [d, ^2J (P, H) = 9 Hz, 9 H, P(CH_3)$_3$], 0.87 [s, exc. P(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, exc. PMe_3, 100.40 MHz): δ = 168.5 (*C*O$_2$CH$_3$), 159.4, 138.3, 135.3, 133.1, 132.9, 120.3, 120.1 [*C*(aryl)], 57.6 (d, *C*H$_2$), 51.9 (CO$_2$*C*H$_3$), 16.6 [exc. P(*C*H$_3$)$_3$], 16.3 [P(*C*H$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, exc. PMe_3, 161.70 MHz): δ = 22.1 [*P*(CH$_3$)$_3$], −61.3 [exc. *P*(CH$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 1718 (s, C=O), 948 (m, P−C−H) cm^{-1}. $C_{26}H_{28}FeNO_4PS_4$ (633.60): calcd. C 49.29, H 4.45, N 2.21, S 20.24; found C 49.10, H 4.67, N 2.21, S 19.99.

[Fe(CO)(pyCO_2MeS$_4$)] (5)

(a) from 6: A suspension of **6**·H_2O·THF (0.070 g, 0.06 mmol) in THF (20 mL) was saturated with CO gas for 3 h and kept under a CO atmosphere for a further 24 h. The resultant red solution was filtered and reduced to one third of its volume. After addition of MeOH (5 mL) the red precipitate which formed was separated by filtration, washed with MeOH (5 mL) and dried in vacuo. Yield: 0.060 g [Fe(CO)(pyCO_2MeS$_4$)] (**5**) (82%).

(b) from 1: A solution of $FeCl_2$·4H_2O (0.083 g, 0.42 mmol) in MeOH (15 mL) was added to a solution of **1**·HCl (0.225 g, 0.42 mmol) and LiOMe (1.25 mmol, 1.25 mL of a 1 M solution in MeOH) in THF (15 mL) under an atmosphere of CO. The mixture was kept under CO gas for a further 2 h. The resultant red precipitate was separated by filtration, washed with MeOH (10 mL) and Et_2O (10 mL) and dried in vacuo. Recrystallization from CH_2Cl_2/Et_2O afforded fine red needles. Yield: 0.174 g [Fe(CO)(pyCO_2MeS$_4$)] (**5**) (71%).^{1}H NMR ($CDCl_3$, 269.60 MHz): δ = 7.67 (m, 4 H, C_6H_3), 7.32 (vt, 1 H, H_γ, pyridine), 7.11 (vd, 2 H, H_β, pyridine), 6.91 (vt, 2 H, C_6H_3), 5.12 (d, 2 H, CH*H*), 4.48 (d, 2 H, C*H*H), 3.84 (s, 6 H, CO_2CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 67.70 MHz): δ = 214.7 (*C*O), 167.5 (*C*O$_2$CH$_3$), 160.2, 157.3, 136.7, 135.6, 135.3, 132.2, 132.1, 121.6, 121.2 [C(aryl)], 56.6 (*C*H$_2$), 51.9 (CO$_2$*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1967 (sh, CO), 1952 (s, CO), 1718 (s, C=O) cm^{-1}. IR (THF): $\tilde{\nu}$ = 1974 (s, CO) cm^{-1}. MS (FD$^+$, CH_2Cl_2): *m*/*z* = 585 [Fe(CO)(pyCO_2MeS$_4$)]$^+$, 557 [Fe(pyCO_2MeS$_4$)]$^+$. C_{24} $H_{19}FeNO_5S_4$ (585.52): calcd. C 49.23, H 3.27, N 2.39, S 21.91; found C 49.46, H 3.21, N 2.37, S 21.66.

[Fe(pyCO_2MeS$_4$)]$_2$ (6): A solution of $FeCl_2$·4H_2O (0.320 g, 1.61 mmol) in MeOH (55 mL) was added dropwise to a solution of **1**·HCl (0.950 g, 1.76 mmol), LiOMe (5.28 mmol, 5.28 mL of a 1 M solution in MeOH) and a small amount of NaBH4 in THF (50 mL) over the course of 3 h. The violet microcrystalline solid which formed was separated by filtration after 45 min, washed with THF (40 mL), MeOH (25 mL) and again with THF (15 mL) and dried in vacuo. Yield: 0.925 g [Fe(pyCO_2MeS$_4$)]$_2$·H_2O·THF (**6**·H_2O·THF) (87%). IR (KBr): $\tilde{\nu}$ = 1711 (s, CO) cm^{-1}. MS (FD$^+$, DMF): *m*/*z* = 557 [Fe(pyCO_2MeS$_4$)]$^+$. Magnetic susceptibility (296 K): μ_{eff} = 0 μ_B. $C_{50}H_{48}Fe_2N_2O_{10}S_8$ (1205.16): calcd. C 49.83, H 4.01, N 2.32, S 21.29; found C 49.59, H 3.85, N 2.34, S 21.37.

[Fe(NO)(pyCO_2MeS$_4$)]BF$_4$ (7)

(a) from 6: $NOBF_4$ (0.023 g, 0.20 mmol) and **6**·H_2O·THF (0.119 g, 0.10 mmol) were suspended in CH_2Cl_2 (15 mL) for 2.5 h. The resultant brown precipitate was separated using a centrifuge, washed with CH_2Cl_2 (5 mL), and recrystallized from acetone. Yield: 0.070 g [Fe(NO)(pyCO_2MeS$_4$)]BF$_4$·0.5 acetone (**7**·0.5 acetone) (50%). $C_{24.5}H_{22}BF_4FeN_2O_{5.5}S_4$ (703.37): calcd. C 41.84, H 3.15, N 3.98, S 18.23; found C 41.95, H 2.93, N 3.96, S 18.18.

(b) from 5: Solid $NOBF_4$ (0.020 g, 0.17 mmol) was added to a solution of **5** (0.100 g, 0.17 mmol) in CH_2Cl_2 (40 mL). The resultant brown precipitate was separated by filtration after 18 h, washed with CH_2Cl_2 (15 mL) and dried in vacuo. Yield: 0.110 g [Fe(NO)(pyCO_2MeS$_4$)]BF$_4$·0.25CH_2Cl_2 (**7**) (93%). ^{1}H NMR (CD_3CN, 269.73 MHz): δ = 7.97 (m, 4 H, C_6H_3), 7.72 (vt, 1 H, H_γ, pyridine), 7.42 (vd, 2 H, H_β, pyridine), 7.39 (vt, 2 H, C_6H_3), 5.49 (d, 2 H, CH*H*), 4.95 (d, 2 H, C*H*H), 3.84 (s, 6 H, CO_2CH_3) ppm. ^{13}C{^{1}H} NMR (CD_3CN,, 67.83 MHz): δ = 166.8 (*C*O-OCH$_3$), 159.0, 154.1, 140.6, 137.1, 134.9, 133.7, 132.0, 127.2, 125.6 [C(aryl)], 56.2 (*C*H$_2$), 53.0 (CO$_2$*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1881 (s, NO), 1712 (s, C=O) cm^{-1}. MS (FD$^+$, CH_3CN): *m*/*z* = 557 [Fe(pyCO_2MeS$_4$)]$^+$. $C_{23.25}H_{19.5}BCl_{0.5}F_4FeN_2O_5S_4$ (695.56): calcd. C 40.15, H 2.82, N 4.03, S 18.44; found C 40.45, H 2.77, N 3.83, S 18.44.

[Fe(NO)(pyCO_2MeS$_4$)] (8): Hydrazine (0.02 mL, 0.66 mmol) was added to a brown solution of **7**·0.25CH_2Cl_2 (0.050 g, 0.07 mmol) in MeOH (15 mL). A red-brown precipitate formed which was separated using a centrifuge after 15 h, washed with MeOH (10 mL) and dried in vacuo. Yield: 0.025 g [Fe(NO)(pyCO_2MeS$_4$)] (**8**) (61%). IR (KBr): $\tilde{\nu}$ = 1720 (s, C=O), 1617 (s, NO) cm^{-1}. MS (FD$^+$, DMF): *m*/*z* = 557 [Fe(pyCO_2MeS$_4$)]$^+$. $C_{23}H_{19}FeN_2O_5S_4$ (587.53): calcd. C 47.02, H 3.26, N 4.77, S 21.83; found C 47.09, H 3.29, N 4.50, S 21.47.

Li_2[Fe(CO)(pyCO_2S_4)] {Li_2[9]}: A solution of **2** (0.336 g, 0.71 mmol) and LiOMe (2.84 mmol, 2.84 mL of a 1 M solution in MeOH) in MeOH (20 mL) was combined with a solution of $FeCl_2{\cdot}4H_2O$ (0.141 g, 0.71 mmol) in MeOH (10 mL). The resultant dark red solution was saturated with CO gas for 1.5 h and filtered after addition of THF (15 mL). The solvent was then removed in vacuo. The so formed light red residue was suspended in THF (50 mL) for 2 h, separated by filtration, washed with THF (30 mL) and dried in vacuo. Yield: 0.497 g Li_2[Fe(CO)(pyCO_2HS_4)]·LiCl·H_2O·3MeOH (Li_2[**9**]·LiCl·H_2O·3MeOH) (96%). ^{1}H NMR (D_2O,): δ = 7.63 (vd, 2 H, C_6H_3), 7.31 (vt, 1 H, H_γ, pyridine), 7.14 (vd, 2 H, H_β, pyridine), 6.95 (m, 4 H, C_6H_3), 4.92 (vd, 2 H, CH*H*), 4.61 (vd, 2 H, C*H*H) ppm. ^{13}C{^{1}H} NMR (D_2O, 100.40 MHz): δ = 217.0 (*C*O), 178.1 (CO_2^{2-}), 158.0, 149.7, 142.5, 137.4, 135.7, 133.0, 127.9, 124.2, 122.7 [C(aryl)], 56.2 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 1969 (s, CO), 1586 (s, CO_2^{2-}), 1392 (s, CO_2^{2-}) cm^{-1}. $C_{25}H_{27}ClFeLi_3NO_9S_4$ (725.85): calcd. C 41.37, H 3.75, N 1.93, S 17.67; found C 41.45, H 3.58, N 1.88, S 17.31.

[Fe(CO)(pyCO_2HS_4)] (10): Hydrochloric acid (1.92 mmol, 7 mL of a 1% solution in H_2O) was added dropwise to a solution of Li_2[**9**]·LiCl·H_2O·3MeOH (0.347 g, 0.48 mmol) in H_2O (25 mL). The resultant light red precipitate was separated using a centrifuge, washed with H_2O (30 mL) and MeOH (40 mL) and dried in vacuo. Yield: 0.255 g [Fe(CO)(pyCO_2HS_4)] (**10**) (95%). ^{1}H NMR ([D_6]DMSO, 269.73 MHz): δ = 12.67 (br., 2 H, COO*H*), 7.90 (vd, 2 H, C_6H_3), 7.61 (vt, 1 H, H_γ, pyridine), 7.44 (m, 4 H, H_β, pyridine + C_6H_3), 6.98 (vt, 2 H, C_6H_3), 4.90 (s, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR ([D_6]DMSO, 67.83 MHz): δ = 216.8 (*C*O), 168.1 (*C*OOH), 156.9, 156.7, 136.4, 135.7, 134.9, 133.3, 130.5, 121.7 [C(aryl)], 55.7 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2974 (m, O−H), 1962 (s, CO), 1681 (s, C=O) cm^{-1}. MS (FD^+, DMSO): *m*/*z* = 529 [Fe(pyCO_2HS_4)]$^+$. $C_{22}H_{15}FeNO_5S_4$ (557.48): calcd. C 47.40, H 2.71, N 2.51, S 23.01; found C 47.68, H 2.59, N 2.58, S 23.21.

[Fe(NO)(pyCO_2HS_4)]BF_4 (11): $NOBF_4$ (0.045 g, 0.39 mmol) and **10** (0.215 g, 0.39 mmol) were suspended in CH_2Cl_2 (40 mL) for 3 days. The resultant brown precipitate was separated by filtration, washed with CH_2Cl_2 (20 mL), dried partially in vacuo and dissolved in MeCN (10 mL). The resultant brown solution was filtered and the solvents evaporated. The brown residue thus formed was dried in vacuo for 60 h. Yield: 0.185 g [Fe(NO)(pyCO_2HS_4)]BF_4 (**11**) (73%). ^{1}H NMR (CD_3CN, 269.72 MHz): δ = 7.98 (vd, 4 H, C_6H_3), 7.70 (vt, 1 H, H_γ, pyridine), 7.38 (m, 4 H, H_β, pyridine + C_6H_3), 5.48 (d, 2 H, CH*H*), 4.93 (d, 2 H, C*H*H) ppm. ^{13}C{^{1}H} NMR (CD_3CN, 67.75 MHz): δ = 158.2, 153.8, 139.8, 136.5, 134.5, 133.1, 131.7, 130.8, 126.4, 124.8 [C(aryl)], 55.2 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2959 (br., O−H), 1900 (s, NO), 1711 (s, C=O) cm^{-1}. MS (FD^+, DMF): *m*/*z* = 529 [Fe(pyCO_2HS_4)]$^+$. $C_{21}H_{15}BF_4FeN_2O_5S_4$ (646.25): calcd. C 39.03, H 2.34, N 4.33; found C 37.94, 2.52 H, N 3.91.

$(NMe_4)_2$[Fe(CO)(pyCO_2S_4)] {$(NMe_4)_2$[9]}: NMe_4OH (0.36 mmol, 0.15 mL of a 25% solution in MeOH) was combined with a suspension of **10** (0.099 g, 0.18 mmol) in MeOH (15 mL) giving a red solution that was filtered and the solvents evaporated. The resultant red residue was dried in vacuo for 15 h. Yield 0.118 g $(NMe_4)_2$[Fe(CO)(pyCO_2S_4)]·$2H_2O$·MeOH [$(NMe_4)_2$[**9**]·$2H_2O$·MeOH) (85%). ^{1}H NMR (D_2O, 269.72 MHz): δ = 7.61 (vdd, 2 H, C_6H_3), 7.33 (vt, 1 H, H_γ, pyridine), 7.15 (vd, 2 H, H_β, pyridine), 6.92 (m, 4 H, C_6H_3), 4.88 (d, 2 H, CH*H*), 4.61 (d, 2 H, C*H*H), 2.96 [s, 24 H, N(CH_3)$_4^+$] ppm. ^{13}C{^{1}H} NMR (D_2O, 67.83 MHz): δ = 217.6 (*C*O), 178.7 (CO_2), 158.5, 150.2, 143.0, 137.9, 136.3, 133.6, 128.4, 124.8, 123.2 [C(aryl)], 57.1 (CH_2), 56.7 [N(CH_3)$_4^+$] ppm. IR (KBr): $\tilde{\nu}$ = 1949 (s, CO), 1580 (s, CO_2^{2-}), 1382 (s, CO_2^{2-}) cm^{-1}. $C_{31}H_{45}FeN_3O_9S_4$ (771.83): calcd. C 48.24, H 5.88, N 5.44, S 16.62; found C 48.09, H 6.13, N 5.64, S 16.59.

[Fe(PMe_3)(pyCO_2HS_4)] (12): A solution of $FeCl_2{\cdot}4H_2O$ (0.090 g, 0.46 mmol) in MeOH (5 mL) was added dropwise to a yellow solution of **2** (0.217 g, 0.46 mmol) and PMe_3 (0.365 mL, 3.65 mmol) in MeOH (10 mL). The resultant red precipitate was separated by filtration after 30 min, washed with MeOH (10 mL) and dried in vacuo. Yield: 0.200 g [Fe(PMe_3)(pyCO_2HS_4)] (**12**) (72%). ^{1}H NMR ([D_6]DMSO, 399.65 MHz, exc. PMe_3): δ = 12.47 (s, 2 H, COO*H*), 7.94 (vd, 2 H, C_6H_3), 7.34 (m, 5 H, C_6H_3 + H_γ, pyridine + H_β, pyridine), 6.89 (vt, 2 H, C_6H_3), 4.78 (d, 2 H, CH*H*), 4.66 (d, 2 H, C*H*H), 1.05 [d, ^2J (P, H) = 8 Hz, 9 H, P(CH_3)$_3$], 0.99 [s, exc. P(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR ([D_6]DMSO, 100.40 MHz, exc. PMe_3): δ = 168.7 (*C*OOH), 159.8, 158.80, 137.1, 134.9, 133.5, 133.2, 129.7, 120.3, 120.1 [C(aryl)], 56.3 (CH_2), 16.0 [exc. P(CH_3)$_3$], 15.7 [P(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR ([D_6]DMSO, 161.70 MHz, exc. PMe_3): δ = 24.1 [*P*(CH_3)$_3$], −61.8 [exc. *P*(CH_3)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2966 (m, O−H), 2612 (w, S−H/O−H), 1701, 1668 (s, CO), 949 (m, P−C−H) cm^{-1}. MS (FD^+, DMSO): *m*/*z* = 529 [Fe(pyCO_2HS_4)]$^+$. $C_{24}H_{24}FeNO_4PS_4$ (605. 54): calcd. C 47.60, H 4.00, N 2.31, S 21.18; found C 47.35, H 4.28, N 2.33, S 20.93.

$(NMe_4)_2$[Fe(PMe_3)(pyCO_2S_4)] {$(NMe_4)_2$[13]}: NMe_4OH (0.19 mmol, 0.076 mL of a 25% solution in MeOH) was combined with a suspension of **12** (0.099 g, 0.18 mmol) in MeOH (15 mL) giving a red solution that was filtered after 10 min. The filtrate was evaporated in vacuo and the resultant dark red residue was dried in vacuo for 15 h. Yield: 0.062 g $(NMe_4)_2$[Fe(PMe_3)(pyCO_2S_4)]·H_2O {$(NMe_4)_2$[**13**]·H_2O} (88%). ^{1}H NMR (CD_3OD, 269.72 MHz, exc. PMe_3): δ = 7.63 (vd, 2 H, C_6H_3), 7.13 (m, 5 H, H_γ, pyridine + H_β, pyridine), 6.93 (vd, 2 H, C_6H_3), 6.79 (vt, 2 H, C_6H_3), 4.82 (br., 2 H, CH*H*), 4.56 (br., 2 H, C*H*H), 1.05 [d, ^2J (P, H) = 9 Hz, 9 H, P(CH_3)$_3$], 1.00 [exc. *P*(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (CD_3OD, 67.83 MHz, exc. PMe_3): δ = 179.0 (CO_2), 161.2, 156.9, 144.7, 136.8, 133.8, 131.9, 126.2, 121.2, 120.7 [C(aryl)], 57.4 (CH_2), 56.1 [N(CH_3)$_4^+$], 17.0 [d, P(CH_3)$_3$], 16.4 [exc. *P*(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (CD_3OD, 161.79 MHz, exc. PMe_3): δ = 22.3 [*P*(CH_3)$_3$], −61.7 [exc. *P*(CH_3)$_3$] ppm. $C_{32}H_{48}FeN_3O_5PS_4$ (769.84): calcd. C 49.93, H 6.28, N 5.46, S 16.61; found C 49.92, H 6.55, N 5.31, S 16.73.

X-ray Structural Determinations of pyCO_2MeS_4−H_2·HCl (1·HCl), [Fe(CO)(pyCO_2MeS_4)] (5), [Fe(pyCO_2MeS_4)]$_2$·H_2O·THF (6·H_2O·THF) and [Fe(PMe_3)(pyCO_2HS_4)]·0.25 MeOH (12·0.25MeOH): Green-yellow single crystals of **1**·HCl were grown by layering a solution of the ligand (0.560 g, 1.04 mmol) in CH_2Cl_2 (40 mL) with *n*-hexane (70 mL) over one week. Red plates of **6**·H_2O·THF were obtained by layering a solution of $FeCl_2{\cdot}4H_2O$ (0.021 g, 0.11 mmol) in H_2O (20 mL) successively with a solution of **1**·HCl (0.058 g, 0.11 mmol) in THF (20 mL), a layer of THF (8 mL), a layer of MeOH (20 mL) and 0.32 mL of a 1 M solution of LiOMe in MeOH. Orange prisms of **5** formed within one week from a saturated CH_2Cl_2 solution which had been layered with the same amount of MeOH. Red blocks of **12**·0.25MeOH were obtained by layering a solution of **1a**·HCl (0.080 g, 0.17) in THF (5 mL) with a solution of $FeCl_2{\cdot}4H_2O$ (0.033 g, 0.17 mmol) and PMe_3 (0.1 mL, 0.1 mmol) in MeOH (3 mL).

Suitable single crystals were embedded either in protective perfluoro polyalkyl ether oil or sealed in a glass capillary under N_2. Intensity data were collected using graphite monochromated Mo-K_α radiation (λ = 71.073 pm) on a Nonius−KappaCCD diffractometer (**6**, **5**) or a Siemens P4 diffractometer (**1**·HCl, **12**·0.25MeOH). Intensity data have been corrected for absorption

Table 4. Crystallographic data for pyCO_2MeS$_4$−H_2·HCl (**1**·HCl), [Fe(CO)(pyCO_2MeS$_4$)] (**5**), [Fe(pyCO_2MeS$_4$)]$_2$·H_2O·THF (**6**·H_2O·THF) and [Fe(PMe_3)(pyCO_2HS$_4$)]·0.25MeOH (**12**·0.25MeOH)

Compound	**1**·HCl	**5**	**6**·H_2O·THF	**12**·0.25MeOH
Formula	$C_{23}H_{22}ClNO_4S_4$	$C_{24}H_{19}FeNO_5S_4$	$C_{50}H_{48}Fe_2N_2O_{10}S_8$	$C_{24.25}H_{25}FeNO_{4.25}PS_4$
M_r [g mol^{-1}]	540.11	585.49	1205.08	613.51
Crystal size [mm]	0.45×0.38×0.25	0.40×0.25×0.14	0.50×0.30×0.10	0.60×0.35×0.20
F(000)	2240	600	622	633
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
Space group	$Fdd2$	$P2_1$	$P\bar{1}$	$P\bar{1}$
a [pm]	3868.1(4)	809.65(2)	972.42(6)	757.9(1)
b [pm]	1015.8(1)	1468.12(4)	1076.16(6)	1247.4(1)
c [pm]	1234.0(1)	1014.06(3)	1460.90(9)	1429.6(1)
α [°]	90	90	91.415(5)	87.76(1)
β [°]	90	100.614(2)	107.943(6)	79.64(1)
γ [°]	90	90	115.724(4)	86.67(1)
V [nm^3]	4.8487(8)	1.18475(6)	1.2877(2)	1.3267(2)
Z	8	2	1	2
$\rho_{calcd.}$ [g cm^{-3}]	1.480	1.641	1.554	1.536
μ [mm^{-1}]	0.534	1.028	0.948	0.977
T [K]	294(2)	100(2)	100(2)	200(2)
θ range [°]	2.11−25.99	4.06−28.00	3.44−26.37	2.22−27.00
Measured refl.	2494	12127	21722	7099
Unique refl.	2377	5145	5247	5780
$R_{int.}$	0.0342	0.0334	0.0573	0.0325
Observed refl.	1440	4881	4101	4348
σ criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Refl. parameters	154	373	364	362
R_1 [$I > 2\sigma(I)$]	0.0583	0.0260	0.0450	0.0455
wR_2 (all data)	0.1512	0.0584	0.1224	0.1165
Absorption correction T_{min}/T_{max}	0.759/0.816	0.770/0.900	0.747/1.000	0.380/0.430
Absolute structure parameters[18]	0.1(2)	0.00(1)	−	−

effects using either Psi-scans (**1**·HCl, **12**·0.25MeOH), multiple scans of equivalent reflections (SADABS,[15] **6**·H_2O·THF) or a numerical Gaussian integration (**5**). The structures were solved by direct methods, and full-matrix least-squares refinements were carried out on F^2 (SHELXTL NT 5.10[16] for **5**, **12** or SHELXTL NT 6.12[17] for **1**, **6**). All non hydrogen atoms were refined anisotropically. Ligand **1** crystallizes as an HCl adduct and the complexes **6** and **12** crystallize with solvent molecules (**6**·H_2O·THF, **12**·0.25MeOH). The MeOH solvate molecule in **12**·0.25MeOH is disordered on a crystallographic inversion center, as is the THF molecule in **6**·H_2O·THF, with two alternative sites for the O atom of the THF molecule. No hydrogen atoms have been taken into account for the structural model of the disordered MeOH of **12**·0.25MeOH and the solvent water of **6**·H_2O·THF. The PMe_3 group in **12** is disordered with two different sites having occupancies of 62(1)% and 38(1)%, respectively. The hydrogen atoms in **1**·HCl, **6**·H_2O·THF and **12**·0.25MeOH were geometrically positioned with isotropic displacement parameters fixed at 1.2 or 1.5 times the U(eq) of the corresponding carbon atom. The positions of the hydrogen atoms in **5** were taken from a difference Fourier synthesis. Their positional parameters were refined with a fixed common isotropic displacement parameter. Table 4 summarizes selected crystallographic data.[19]

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