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Synthesis and Molecular Structure of Carbonyl Derivatives of Iron(II) Thiolates Containing Nitrogen-donor Ligands

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Abstract

Several carbonyl derivatives of iron(II) thiolates containing N-donor ligands with the general formula $FeS_2N_2(CO)_2$ were prepared in methanol solution starting from $FeSO_4 \cdot 7H_2O$, the appropriate thiol (S) and nitrogen-donor ligand (N), carbon monoxide and a base.

The structures of two representatives $Fe(SC_6H_4\text{-}NH_2\text{-}o)_2(CO)_2$ (**1**) and $Fe(SPh)_2(H_2NC_2H_4NH_2)(CO)_2$ (**2**) were determined. Complex **1** crystallizes with one molecule of THF in the triclinic space group $P1$, $a = 5.659(3)$, $b = 8.960(6)$, $c = 10.624(6)$ Å, $\alpha = 105.15(5)$, $\beta = 103.23(5)$, $\gamma = 94.35(5)°$, $V = 500.86$ Å^3, $Z = 1$, $D_{calc} = 1.43$ g cm^{-3}. Complex **2** crystallizes in the monoclinic space group $P2_1/c$, $a = 11.739(2)$, $b = 9.725(2)$, $c = 15.868(2)$ Å, $\beta = 101.583(8)°$, $V = 1774.6$ Å^3, $Z = 4$, $D_{calc} = 1.44$ g cm^{-3}. Final agreement factors, $R = 0.0300$, $R_w = 0.0304$ (1787 reflections) for **1**; $R = 0.0368$, $R_w = 0.0369$ (2147 reflections) for **2**; the absolute configuration of **1** was determined. The octahedral complexes contain the two CO ligands in *cis* position and the coordinated N atoms are *trans* to the CO groups. A necessary condition for the stability of such complexes is the presence of at least one chelating ligand; all complexes lose CO on heating and this reaction is (in part) reversible.

Introduction

Absorption of CO under mild conditions is a useful and convenient method for the preparation of thiolato iron(II) carbonyls from solutions of Fe(II) salts containing the necessary ligands and a base. The compounds synthesized by this method all contain two-electron donor S, N, or P ligands in addition to the thiolato and CO groups [1–7].

Recently we reported the synthesis of analogous iron(II) dicarbonyl complexes containing xanthate, dithiocarbamate and dithiophosphate ligands under similar conditions [8]. In continuation of this research we prepared using the same method several new iron(II) carbonyl complexes containing thiolato and N-donor ligands and report our results here.

Two types of complexes were prepared and characterized: complexes of type **A** with the general formula $Fe(S\hat{}N)_2(CO)_2$ where $(S\hat{}N)$ represents a ligand containing a thiolato and an amino group; and complexes of type **B** having the general formula $Fe(SPh)_2(N\hat{}N)(CO)_2$ which contain a bidentate N-N ligand $(N\hat{}N)$.

Experimental

Preparation of $Fe(S\hat{}N)_2(CO)_2$ *(type A) Complexes*

$Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2$ *(1) and* $Fe(SCH_2CH(NH_2)COOEt)_2(CO)_2$

To 2.0 mmol (556 mg) $FeSO_4 \cdot 7H_2O$ dissolved in 15 ml MeOH, 4.0 mmol $HS\hat{}N$ ligand and 4.0 mmol (557 μl) Et_3N in 15 ml MeOH were added dropwise with stirring under CO. During continued stirring CO was absorbed and the complexes **1** as well as $Fe(SCH_2CH(NH_2)COOEt)_2(CO)_2$ precipitated from the reaction mixture as pink and orange microcrystalline solids, respectively. After 4 h the solids were filtered off, washed with a small amount of cold MeOH and dried *in vacuo*. The filtrates yielded additional amounts of the products upon cooling to −18 °C. Recrystallization of **1** from THF/hexane by the slow diffusion method under CO yielded **1**·THF as large red prisms. Most of the crystals obtained were composed of several layers but some smaller species suitable for X-ray structure analysis could be selected.

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TABLE 1. Experimental and crystal data for X-ray analysis of **1**·THF and **2**[a]

	Complex **1**·THF	Complex **2**
Space group	$P1$ (C_1^1, No. 1)	$P2_1/c$ (C_{2h}^5, No. 14)
a (Å)	5.659(3)	11.739(2)
b (Å)	8.960(6)	9.725(2)
c (Å)	10.624(6)	15.868(2)
α (°)	105.15(5)	90.00
β (°)	103.23(5)	101.583(8)
γ (°)	94.35(5)	90.00
V (Å^3)	500.86	1774.6
Molecular weight	432.36	386.29
Z	1	4
D_{calc} (g cm^{-3})	1.43	1.44
μ(Mo Kα) (cm^{-1})	9.15	10.25
Crystal dimensions (approx.) (mm)	0.4 × 0.3 × 0.6	0.2 × 0.2 × 0.2
Diffractometer	Nicolet R3	Philips PW1100
Radiation	Mo Kα (graphite monochr., λ = 0.7107 Å)	
Scan technique	ω	$\theta-2\theta$
Scan width (°)	1.80	1.20
Scan speed (° s^{-1})	1.5–15.0	2
Scan range (θ) (°)	1–25	1–25
Background	0.5[b]	20 s
Collected reflections	1980	3623
Standard reflections	1 every 50 reflections	2 every 120 min
Reflections with $F > 6$ (F)	1787	2147
Final R	0.0300	0.0367
Final R_w	0.0304	0.0369

[a] Here and in the subsequent Tables the e.s.d.s are in parentheses. [b] Ratio of total background time to scan time.

$Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2 \cdot THF$ (**1**·THF), yield 337 mg (39%). *Anal.* Found: C, 50.16; H, 4.65; N, 6.49. Calc.: C, 50.02; H, 4.66; N, 6.48%.

$Fe(SCH_2CH(NH_2)COOEt)_2(CO)_2$, yield 530 mg (65%). *Anal.* Found: C, 35.01; H, 4.78; N, 6.76. Calc.: C, 35.3; H, 4.94; N, 6.86%.

$Fe(SCH_2CH_2NH_2)_2(CO)_2$

To 2.0 mmol $FeSO_4 \cdot 7H_2O$ (556 mg) dissolved in 15 ml MeOH, 2.0 mmol (227 mg) $HSCH_2CH_2NH_2 \cdot HCl$ and 4.0 mmol Et_3N (557 μl) in 20 ml MeOH were added dropwise under CO. As the stirring was continued a pale yellow substance not containing carbonyl ligands (IR) was formed. After 3 h of stirring the precipitate was removed by filtration and the filtrate was cooled to –18 °C. The deposited orange crystals of $Fe(SCH_2CH_2NH_2)_2(CO)_2$ were filtered, washed with a small amount of cold MeOH and dried *in vacuo*.

Yield 103 mg (19.5%). *Anal.* Found: C, 27.38; H, 4.51; N, 10.37. Calc.: C, 27.28; H, 4.58; N, 10.60%.

Preparation of $Fe(SPh)_2(N\hat{}N)(CO)_2$ (Type *B*) Complexes

To a MeOH solution (15 ml) of 1.0 mmol $FeSO_4 \cdot 7H_2O$ (278 mg), 2.0 mmol NaSPh (264 mg) and 1.0 mmol N^N ligand dissolved in 15 ml MeOH were added dropwise under CO. While stirring was continued CO was absorbed and the color of the solution became red. After 4 h the Na_2SO_4 precipitate was filtered off and the filtrate was cooled to –18 °C under CO. After a few days the product was filtered, the red crystals were washed with a small amount of cold MeOH and dried *in vacuo*.

$Fe(SPh)_2(H_2NCH_2CH_2NH_2)(CO)_2$ (**2**), yield 129 mg (33%). *Anal.* Found: C, 49.28; H, 4.55; N, 6.97. Calc: C, 49.24; H, 4.65; N, 7.17%.

$Fe(SPh)_2(bpy)(CO)_2$, yield 180 mg (37.5%). *Anal.* Found: C, 59.28; H, 3.77; N, 5.58. Calc.: C, 59.26; H, 3.73; N, 5.75%. $Fe(SPh)_2(phen)(CO)_2$, yield 178 mg (35%). *Anal.* Found: C, 60.7; H, 3.59; N, 5.41. Calc.: C, 61.18; H, 3.52; N, 5.48%.

Collection and Reduction of X-ray Data

The representative complexes studied by X-ray analysis were **1**·THF and **2**. The values of the cell parameters and the experimental conditions used during the structure determinations are reported in Table 1 for both compounds. The lattice parameters were obtained from the refinement of 25 angles of accurately centered reflections. The check of the standard reflections showed no significant decrease. No absorption correction was applied. A secondary extinction correction was applied to the complex **2**. The fractional coordinates of the non-hydrogen atoms are listed in Tables 2 and 3 for **1** and **2**, respectively.

TABLE 2. Fractional atomic coordinates referred to one molecule for **1**·THF

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe	1.0	0.0	0.0
S(1)	0.68110(19)	0.09337(14)	−0.11717(12)
S(2)	1.32958(19)	−0.06886(14)	0.13219(12)
N(1)	1.2051(7)	0.2046(4)	0.0156(4)
N(2)	0.9162(7)	0.1038(4)	0.1763(4)
C(1)	0.8168(8)	−0.1773(5)	−0.0160(5)
C(2)	1.0704(9)	−0.0935(5)	−0.1519(5)
C(3)	0.8542(8)	0.1444(5)	−0.1483(4)
C(4)	0.7516(9)	0.3225(5)	−0.2409(5)
C(5)	0.8955(6)	0.4390(6)	−0.2637(5)
C(6)	1.1397(10)	0.4792(6)	−0.1974(6)
C(7)	1.2433(8)	0.4042(5)	−0.1054(5)
C(8)	1.1009(7)	0.2865(4)	−0.0821(4)
C(9)	1.2518(7)	−0.0121(5)	0.2868(4)
C(10)	1.3808(8)	−0.0465(5)	0.4013(5)
C(11)	1.3112(10)	−0.0045(6)	0.5197(5)
C(12)	1.1099(10)	0.0738(6)	0.5274(5)
C(13)	0.9799(9)	0.1090(5)	0.4152(5)
C(14)	1.0493(7)	0.0672(4)	0.2950(4)
C(15)	1.1381(20)	0.5153(9)	0.3962(8)
C(16)	0.9078(23)	0.5795(11)	0.4073(9)
C(17)	0.8113(16)	0.6202(9)	0.2785(8)
C(18)	0.9655(15)	0.5409(7)	0.1877(7)
O(1)	−0.2969(7)	−0.2937(4)	−0.0323(4)
O(2)	0.1013(8)	−0.1577(4)	−0.2533(4)
O(3)	1.1056(9)	0.4449(4)	0.2545(4)

TABLE 3. Fractional atomic coordinates referred to one molecule for **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe	0.12566(4)	0.24450(5)	0.06197(3)
S(1)	0.32314(8)	0.19415(13)	0.09916(6)
S(2)	−0.06979(8)	0.29219(11)	0.00488(6)
N(1)	0.1651(3)	0.3753(4)	−0.0286(2)
N(2)	0.1173(3)	0.1057(4)	−0.0348(2)
C(1)	0.1355(3)	0.3773(4)	0.1385(2)
C(2)	0.0979(3)	0.1206(4)	0.1359(2)
C(3)	0.1383(4)	0.3094(6)	−0.1149(3)
C(4)	0.1723(4)	0.1618(5)	−0.1034(3)
C(5)	0.3691(2)	0.1851(2)	0.2130(2)
C(6)	0.3746(3)	0.0601(4)	0.2542(3)
C(7)	0.4192(4)	0.0510(5)	0.3427(3)
C(8)	0.4607(4)	0.1660(5)	0.3885(3)
C(9)	0.4557(4)	0.2904(5)	0.3472(3)
C(10)	0.4097(3)	0.3013(4)	0.2604(3)
C(11)	−0.1645(3)	0.2506(4)	0.0751(2)
C(12)	−0.1398(3)	0.2744(4)	0.1628(3)
C(13)	−0.2181(4)	0.2398(4)	0.2139(3)
C(14)	−0.3236(4)	0.1839(5)	0.1779(4)
C(15)	−0.3511(4)	0.1617(5)	0.0907(4)
C(16)	−0.2725(3)	0.1938(4)	0.0389(3)
O(1)	0.1409(3)	0.4636(3)	0.1875(2)
O(2)	0.0804(2)	0.0390(3)	0.1837(2)

Solution and Refinement of the Structures

Complex 1

Some peaks of the Patterson map allowed the localization of the Fe and S atoms, then subsequent difference Fourier-syntheses revealed the C, N and O atoms. The resolution and refinement led to one chiral molecule in the unit cell. The values of $R = 0.0300$, $R_w = 0.0304$, and $R = 0.0356$, $R_w = 0.0379$ were reached, respectively, at the end of two refinement cycles corresponding to the two enantiomers [9]. The great difference (>20%) between the two refinements is sufficiently significant. Nevertheless the structure factors calculated from the two models were compared and some suitable pairs were selected for the Bijvoet test [10] (from nearly 50 measured pairs, some relevant examples are reported in Table 4). Both tests selected the initial set of coordinates as the correct model for this crystal of the conglomerate.

TABLE 4. Some selected Bijvoet pairs used in the determination of the absolute configuration of **1**·THF

Reflection	Measured[a]	Calculated[b]
0 1 −9	1.07	1.05
1 −1 −8	1.22	1.18
2 1 8	0.89	0.92
3 2 −9	1.16	1.14
1 6 −9	0.89	0.90
2 2 −8	1.36	1.36
1 −1 −7	1.09	1.08
1 2 −7	1.20	1.21
0 8 −7	0.80	0.79
1 6 6	0.74	0.77
2 −5 −6	1.12	1.11
5 2 −6	0.86	0.86
3 −3 −5	1.19	1.17
3 0 −5	1.29	1.26
1 4 −5	0.82	0.82
1 5 4	1.28	1.29
2 −5 −4	1.26	1.28
3 1 4	0.85	0.85
4 4 −4	0.85	0.84
4 2 3	0.76	0.79
2 6 −4	0.70	0.73
3 0 −3	1.33	1.29
4 4 −3	0.82	0.84
1 2 2	0.80	0.81
2 2 −2	0.82	0.84
1 2 1	0.85	0.87

[a] Measured ratio $F(+++)/F(---)$. [b] Calculated ratio $F(+++)/F(---)$.

Complex 2

The three-dimensional Patterson map and its Harker sections gave the positions of the iron atom, and the subsequent difference Fourier-syntheses allowed the localization of the remaining atoms.

The weighting scheme for both complexes was $w = 1/(\sigma(F)^2 + aF^2)$ where a was varied in order to obtain a satisfying constancy of the $\Sigma w\Delta^2$ value in various ranges of $|F_o|$ and senθ/λ. On the difference maps of the last refinement cycles the peaks corresponding to some hydrogen atoms appeared coincident to the calculated positions. So all the calculated hydrogen atoms were introduced. All atoms (H excluded) were allowed to vary anisotropically. Unique isotropic thermal parameters were used for blocks of H atoms with common features (e.g. hydrogens of phenyl groups, of amino groups etc.) All calculations associated with the solution and refinement were carried out with SHELX-76 [11].

Results and Discussion

Synthesis of Complexes of Type A

Methanolic solutions of $FeSO_4 \cdot 7H_2O$ containing $HSC_6H_4NH_2$-*o*, $HSCH_2CH_2NH_2$, or L-$HSCH_2CH(NH_2)COOEt$ and Et_3N as a base rapidly absorbed CO at room temperature and atmospheric pressure and yielded the complexes of $Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2$, (**1**), $Fe(SCH_2CH_2NH_2)_2(CO)_2$ and $Fe(SCH_2CH(NH_2)COOEt)_2$ as pink or orange solids according to eqn. (1)

$$Fe^{2+} + 2HS\hat{\ }N + 2Et_3N + 2CO \longrightarrow Fe(S\hat{\ }N)_2(CO)_2 + 2Et_3NH^+ \qquad (1)$$

In the case of $HSC(CH_3)_2CH(NH_2)COOH$ the product could be characterized only in methanol solution. Carbon monoxide uptake was practically stoichiometric in all cases.

Reacting Fe^{2+} and *o*-$H_2NC_6H_4S^-$ in the absence of CO, the already known paramagnetic $Fe(SC_6H_4NH_2\text{-}o)_2$ [12] was formed which is practically insoluble and thought to have polymeric structure. This substance reacted in a methanolic slurry with CO and gave the same dicarbonyl complex as obtained by the direct procedure according to eqn. (1). Analogous CO-free complexes may be the intermediates of carbonyl formation in the other cases too.

Synthesis of Complexes of Type B

These compounds were prepared in a similar way in MeOH solution from $FeSO_4 \cdot 7H_2O$, PhSNa, the bidentate N ligand, and CO according to eqn. (2)

$$Fe^{2+} + 2PhS^- + N\hat{\ }N + 2CO \longrightarrow Fe(SPh)_2(N\hat{\ }N)_2(CO)_2 \qquad (2)$$

The complexes $Fe(SPh)_2(H_2NCH_2CH_2NH_2)_2(CO)_2$ (**2**), $Fe(SPh)_2(bpy)_2(CO)_2$ and $Fe(SPh)_2(phen)_2(CO)_2$ (bpy: 2,2′-bipyridine; phen: 1,10-phenanthroline) could be isolated as crystalline solids. No reaction was observed in the case of $Me_2NCH_2CH_2NMe_2$ (probably because of steric reasons) and the complex containing $H_2N(CH_2)_3NH_2$ as bidentate N ligand proved to be very unstable. If aliphatic thiols were used instead of thiophenol or if monodentate amines were used as potential ligands, other types of complexes were formed which will be discussed in a separate publication.

Infrared Spectra

The IR spectra of the complexes in the νCO region (Table 5) show two absorptions of approximately equal intensity in the 2030–1950 cm^{-1} region and are thus very similar to the spectra of $Fe(cys)_2(CO)_2$ (cysH = L-cysteine) and the Fe(II) thioether–thiolato dicarbonyl complexes $Fe(SC_6H_4SMe\text{-}o)_2(CO)_2$ [3] and $Fe(S\hat{\ }S\hat{\ }S\hat{\ }S)(CO)_2$ [4] ($HS\hat{\ }S\hat{\ }S\hat{\ }SH$ = 1,2-bis(2-thiol-1-phenylthio)ethane). On the basis of these informations it may be expected that the carbonyl ligands occupy *cis* positions within the octahedral complexes. This assumption was verified by the X-ray structure determination of two representative complexes (one of type **A** and one of type **B**; *vide infra*). In addition, the very simple spectra prove that the compounds consist of only one stereoisomer.

TABLE 5. IR data of $Fe(S\hat{\ }N)_2(CO)_2$ (type A) and $Fe(SPh)_2(N\hat{\ }N)(CO)_2$ (type B) complexes

Type of complex	HS^N or N^N	νCO (cm^{-1}) (in MeOH)	
A	$HSCH_2CH_2NH_2$	2020	1963
A	$HSCH_2CH(NH_2)COOEt$	2024	1968
A	$HSC(CH_3)_2CH(NH_2)COOH$	2015	1956
A	*o*-$HSC_6H_4NH_2$	2021	1963
B	$H_2NCH_2CH_2NH_2$	2026	1973
B	2,2′-bipyridine	2029	1983
B	1,10-phenanthroline	2029	1985

Structure of $Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2\cdot THF$ ($1\cdot THF$)

Crystals were grown from a THF solution. Complex **1** and molecules of solvent cocrystallize in a 1:1 ratio. The structure of the molecule is shown in Fig. 1, where also the THF molecule is reported. Selected bond distances and angles are listed in Table 6, with their estimated standard deviations.

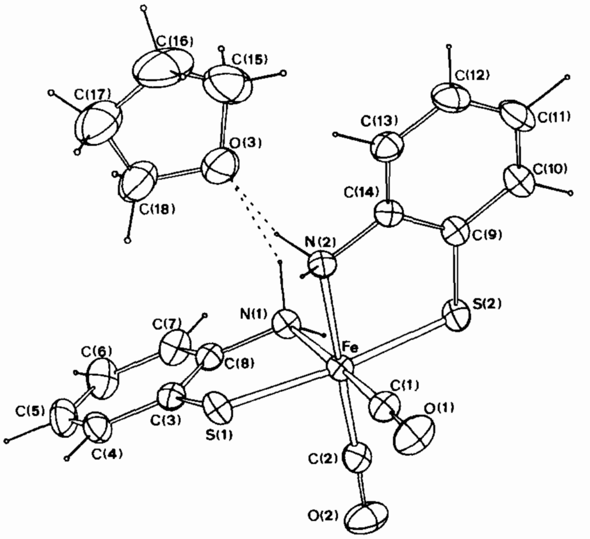

Fig. 1. ORTEP plot of $Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2\cdot THF$ ($1\cdot THF$) with 36% ellipsoids.

As can be seen, the CO ligands occupy *cis* positions within the octahedral environment of the Fe atom, the *o*-aminothiophenolato ligands are arranged in a way which puts the S atoms in *trans*, and the N atoms in *cis* positions. The molecule possesses therefore C_2 symmetry, the twofold axis lying between the two CO and the two NH_2 groups. Since a molecule having C_2 symmetry is chiral and only one enantiomer is present in the crystal (see 'Experimental'), a spontaneous resolution due to conglomerate crystallization is suggested [13].

The absolute configuration at iron was determined to be Δ by the technique of anomalous dispersion [9, 10] and confirmed by comparing Bijvoet differences as described in 'Experimental'.

An explanation of the occurrence of the conglomerate crystallization may be the presence of O..H–N bonds between the THF molecule and the complex, which keep the molecule of THF within the space between the two pentaatomic rings where a crowding of hydrogen atoms is realized (Fig. 1). The corresponding values are: 2.18(3) and 2.08(3) Å for $O..H_{N(1)}$ and $O...H_{N(2)}$ distances and 3.062(6) and 2.990(5) Å for O...N(1) and O...N(2) distances, respectively.

We wished to verify the chirality of the crystals by an independent way and tried to measure the CD spectrum of the THF solution of a single crystal but could not observe any optical activity. The most plausible explanation for this negative result may be a very rapid racemization of the complex in solution. It should be mentioned here, that the structure of **1** is in accord with the observation of Tomita *et al.* [14] who reported an unusually large specific optical rotation for the complex $Fe(cys)_2(CO)_2$ which cannot be explained by the chirality of the HS^N ligand alone but suggests the existence of a configurational effect too.

Two types of intermolecular links, both involving the H atoms of the amino groups, are observed: the above mentioned bonds between one half of the H atoms and the oxygen atoms of THF and between the other half of the H atoms and the S atoms of molecules shifted +1 and −1 along the *x* axis. In the latter case the distances S...H are 2.47(2) and 2.44(2) Å, respectively (value classified as H bonds in ref. 15), with angles around S in the range of 108–118°. Other intermolecular links involve the oxygen atoms of the CO groups and the hydrogen atoms of the phenyls with distances in the range of 2.6–2.8 Å.

Inside the octahedral coordination around Fe, only the C–Fe–N bonds are strictly aligned, while the S atoms (S–Fe–S angle of 174.3°) feel the effects of the constrain in the pentaatomic ring, where the S–Fe–N angle is smaller than 90° (85.7°). As a consequence of the presence of rings, among the three theoretical planes that define an exact octahedral coordination, two are strongly (C(1), Fe, N(1), S(1), S(2) and C(2), Fe, N(2), S(1), S(2)) and one is slightly (C(1), C(2), Fe, N(1), N(2) $\chi^2 = 14.2$) puckered. The aromatic rings of the $C_6H_4SNH_2$ ligands are planar, but the N and S atoms fall significantly outside this plane. This is in contrast to that found in the other known aminothiophenol complex [16], where a close planarity is observed for the C_6NS atoms. This behaviour is probably a consequence of the above mentioned intermolecular bonds involving the S and NH_2 groups. Notwithstanding the puckering of the FeSCCN rings the C–S bonds are slightly shorter than single bonds and a small delocalization N–C–C–S is probably present. Between the two *o*-aminothiophenol ligands no significant difference in distance or angle values occurs.

Comparing **1** with other compounds containing pentaatomic $FeSC_2N$ rings [16, 17], the best agreement with regard to angles and bond distances is observed with $Fe_2(CO)_6(C_6H_5SNH)$, though the ligand in this latter complex is bonded to an Fe_2 unit.

Structure of $Fe(H_2NCH_2CH_2NH_2)(SPh)_2(CO)_2$ (2)

Crystals suitable for X-ray structure determination were grown from methanol. Relevant distances and angles are listed in Table 6. As shown in Fig. 2 the CO ligands occupy *cis* and the thiophenolato ligands *trans* positions in the pseudooctahedral complex: the

TABLE 6. Selected values of interatomic distances (Å) and angles (°) for **1**·THF and **2**

Complex **1**·THF			
Fe–S(1)	2.293(1)	S(1)–Fe–N(2)	90.1(1)
Fe–S(2)	2.294(1)	S(1)–Fe–C(1)	93.4(2)
Fe–N(1)	2.040(3)	S(1)–Fe–C(2)	90.3(2)
Fe–N(2)	2.040(4)	S(2)–Fe–N(1)	90.4(1)
Fe–C(1)	1.776(4)	S(2)–Fe–N(2)	85.9(1)
Fe–C(2)	1.762(5)	S(2)–Fe–C(1)	90.8(2)
S(1)–C(3)	1.755(4)	S(2)–Fe–C(2)	93.7(2)
S(2)–C(9)	1.754(4)	N(1)–Fe–N(2)	89.5(2)
N(1)–C(8)	1.466(5)	N(1)–Fe–C(1)	178.9(2)
N(2)–C(14)	1.445(6)	N(1)–Fe–C(2)	91.6(2)
C(1)–O(1)	1.131(5)	N(2)–Fe–C(1)	90.7(2)
C(2)–O(2)	1.139(5)	N(2)–Fe–C(2)	178.8(2)
C(3)–C(4)	1.398(6)	C(1)–Fe–C(2)	88.2(2)
C(3)–C(8)	1.385(6)	Fe–S(1)–C(3)	97.9(1)
C(4)–C(5)	1.379(7)	Fe–S(2)–C(9)	98.5(1)
C(5)–C(6)	1.372(7)	Fe–N(1)–C(8)	115.1(3)
C(6)–C(7)	1.375(7)	Fe–N(2)–C(14)	116.2(3)
C(7)–C(8)	1.385(6)	Fe–C(1)–O(1)	176.3(4)
C(9)–C(10)	1.390(6)	Fe–C(2)–O(2)	175.8(4)
C(9)–C(14)	1.401(6)	S(1)–C(3)–C(4)	121.9(3)
C(10)–C(11)	1.371(7)	S(1)–C(3)–C(8)	119.7(3)
C(11)–C(12)	1.390(7)	N(1)–C(8)–C(3)	117.7(3)
C(12)–C(13)	1.375(7)	N(1)–C(8)–C(7)	121.1(4)
C(13)–C(14)	1.388(6)	S(2)–C(9)–C(10)	122.2(3)
S(1)–Fe–S(2)	174.3(0)	S(2)–C(9)–C(14)	119.2(3)
S(1)–Fe–N(1)	85.5(1)		
Complex **2**			
Fe–S(1)	2.326(1)	N(2)–Fe–C(2)	93.5(2)
Fe–S(2)	2.338(1)	C(1)–Fe–C(2)	92.2(2)
Fe–N(1)	2.041(3)	Fe–S(1)–C(5)	110.6(1)
Fe–N(2)	2.032(3)	Fe–S(2)–C(11)	113.7(1)
Fe–C(1)	1.760(4)	Fe–N(1)–C(3)	110.1(3)
Fe–C(2)	1.756(4)	Fe–N(2)–C(4)	110.5(3)
S(1)–C(5)	1.783(3)	Fe–C(1)–O(1)	179.3(4)
S(2)–C(11)	1.772(3)	Fe–C(2)–O(2)	179.4(4)
N(1)–C(3)	1.488(6)	N(1)–C(3)–C(4)	107.5(4)
N(2)–C(4)	1.477(5)	N(2)–C(4)–C(3)	107.4(4)
C(3)–C(4)	1.491(7)	S(1)–C(5)–C(6)	120.0(3)
C(1)–O(1)	1.137(4)	S(1)–C(5)–C(10)	120.6(3)
C(2)–O(2)	1.145(1)	C(6)–C(5)–C(10)	119.1(4)
S(1)–Fe–S(2)	172.1(0)	C(5)–C(6)–C(7)	120.3(4)
S(1)–Fe–N(1)	87.4(1)	C(6)–C(7)–C(8)	120.2(4)
S(1)–Fe–N(2)	86.9(1)	C(7)–C(8)–C(9)	119.4(4)
S(1)–Fe–C(1)	93.2(1)	C(8)–C(9)–C(10)	121.1(4)
S(1)–Fe–C(2)	89.7(1)	C(5)–C(10)–C(9)	120.0(4)
S(2)–Fe–N(1)	87.0(1)	S(2)–C(11)–C(12)	124.3(3)
S(2)–Fe–N(2)	86.8(1)	S(2)–C(11)–C(16)	117.6(3)
S(2)–Fe–C(1)	92.6(1)	C(12)–C(11)–C(16)	118.1(4)
S(2)–Fe–C(2)	95.5(1)	C(11)–C(12)–C(13)	121.3(4)
N(1)–Fe–N(2)	82.2(1)	C(12)–C(13)–C(14)	120.2(5)
N(1)–Fe–C(1)	92.0(2)	C(13)–C(14)–C(15)	119.6(4)
N(1)–Fe–C(2)	175.0(2)	C(14)–C(15)–C(16)	120.7(4)
N(2)–Fe–C(1)	174.3(2)		

ethylenediamine is coordinated *trans* to the CO groups. The environment of the Fe atom possesses C_2 symmetry owing to the conformation of the chelate ring, but the chirality is lost if the compound is dissolved in a solvent; in the unit cell both configurations are present.

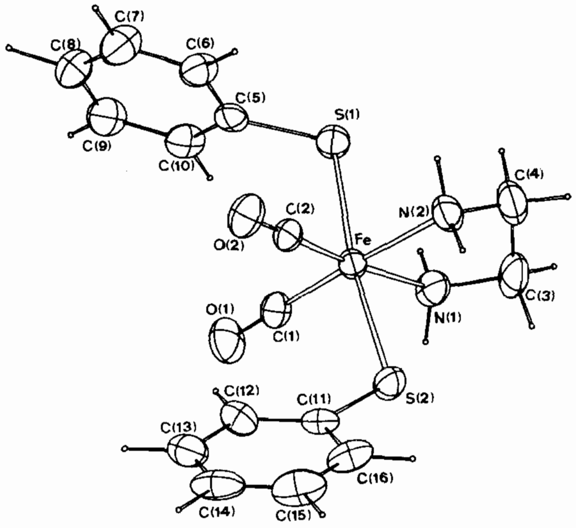

Fig. 2. ORTEP plot of $Fe(SPh)_2(H_2NC_2H_4NH_2)(CO)_2$ (2) with 36% ellipsoids.

The geometry around Fe is not exactly octahedral owing to the non-planarity of the C(1)C(2)FeN(1)N-(2) core, to the angle S(1)–Fe–S(2) being quite different from 180° and to the distortion introduced by the five-membered FeN(1)N(2)C(3)C(4) ring.

The phenyl rings of the thiolato ligands, both on the side of the CO groups, reflect the two situations that normally occur in phenylthiolato compounds [18]. One of the phenyl rings is perpendicular (89°) to the corresponding FeS(1)C(5) plane, while the other one is nearly parallel (14°) to the FeS(2)C(11) plane. In the former case the least hindered situation [19] is realized with no interaction between the phenyl group and the other equatorial ligands (in this case the CO groups). Figure 3 shows clearly the situation of the thiolato ligands.

One *ortho* hydrogen atom of the parallel phenyl group interacts with the oxygen atom of one CO group; the $H_{C(12)}$...O(1) distance (2.727(5) Å) is of the order of the sum of the van der Waals radii, while the distance of H from O(2) is nearly 3.2 Å. Contemporarily a close intramolecular contact between S(2) and the H atom of an amino group occurs (2.61 Å).

Some angle values (Fig. 3) clearly show the effect of these interactions: comparing the Fe–S–C_{Ph} angles, the difference is greater than 306; the angles around C(5) are strictly 120°, while around the C(11) atom there is a significant difference (larger than 20σ) in the angle values. At the same time different Fe–S distances (12σ) occur, while the S–C_{Ph} difference is not significant. The S(1)–Fe–S(2) angle value of 172° is probably a consequence of repulsions.

An accurate analysis [19] of similar effects was reported for the $M(thiol)_4{}^{2-}$ anions, where intramolecular H...S repulsions were found.

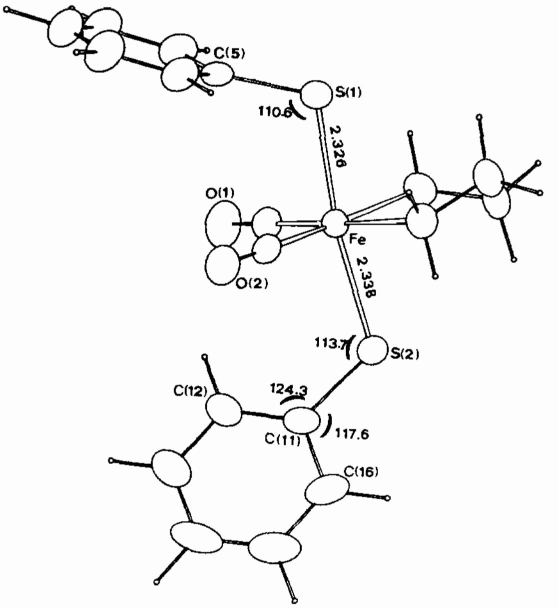

Fig. 3. ORTEP plot of $Fe(SPh)_2(H_2NC_2H_4NH_2)(CO)_2$ (2) showing the geometry of the thiophenol ligands and the $H_{C(12)}$...O(1) interaction.

Reversibility of CO Absorption

Absorption of CO was (at least partly) reversible in all the cases studied in this work. Dissociation of the complexes in solution was easily achieved either by warming or under vacuum; the process could be conveniently followed by IR spectrometry. The release and uptake of CO could be repeated several times but the process was often accompanied by irreversible decomposition reactions leading to a gradual decrease in the concentration of the dicarbonyl complexes. A more quantitative study of these reactions is presently under way in our laboratories.

Supplementary Material

Listing of observed and calculated structure factors (22 pages), thermal anisotropic and isotropic parameters (3 pages), and fractional coordinates of the hydrogen atoms (4 pages) are available from the authors (G.G. or L.M.) on request.

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