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SULPHURATING AND COORDINATING PROPERTIES OF N,N′-THIOBISMORPHOLINE TOWARDS IRON CARBONYLS

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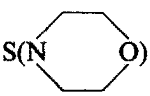
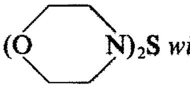
Abstract—The reactions of N,N′-thiobismorpholine,  $S(N\quad O)_2$, with $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{11}$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$ were examined. Thiobismorpholine undergoes desulphurization towards $Fe(CO)_5$ with formation of $Fe_3(CO)_9S_2$, while the novel complex  $Fe(CO)_4S(N\quad O)_2$ was isolated and characterized from the reaction with $Fe_2(CO)_9$. On the other hand, thiobismorpholine is somewhat unreactive towards $Fe_3(CO)_{11}$ but it undergoes S—N fission with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$.

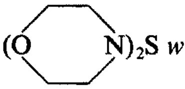
N,N′-thiobisamines, $(R_2N)_2S$, are known to be quite unreactive compounds.[1] They react neither with water nor with alcohols, but in the presence of H^+, ion metals or Lewis acid, redox[2,3] and substitution processes occur.[4] The low reactivity of N,N′-thiobisamines has been frequently explained by the diminished nucleophilicity of the sulphur and nitrogen atoms, arising from double bond character in the S—N linkage.[5] In spite of the expected coordinative properties arising from the lone electron pairs on the sulphur and nitrogen atoms the only metal complexes with N,N′-thiobisamines as ligands reported are $[M(CO)_5S(NR_2)_2]$ (M = Cr, Mo, W).[6] As part of our investigation of the coordinative properties of S^{II}—N compounds,[6,7] we now report the reaction of N,N′-thiobismorpholine with iron pentacarbonyl, enneacarbonyldiirons and triiron dodecacarbonyl.

RESULTS AND DISCUSSION

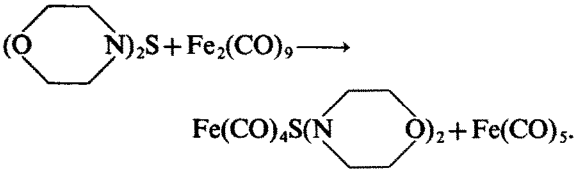
Reaction of  $(O\quad N)_2S$ *with* $Fe(CO)_5$

When iron pentacarbonyl was irradiated (UV) with N,N′-thiobismorpholine in methanol for 3 h at room temperature, dark red needles were produced. This compound was identified by elemental analysis, IR and mass spectroscopy as $Fe_3S_2(CO)_9$.[8] Its IR spectra were identical with those reported in the literature.[8–10] The mass spectrum of this compound showed the parent ion and the fragments arising from stepwise loss of all the carbonyl groups. Peaks at m/z 176, 144 and 120, corresponding to $Fe_2S_2^+$, Fe_2S^+ and FeS_2^+ fragments, were also observed.

The sulphur-transfer behaviour of N,N′-thiobismorpholine toward iron pentacarbonyl is unexpected but not surprising in view of the desulphurization behaviour shown by other organic sulphides toward iron carbonyls.[9,10] Furthermore, the compound $Fe_3S_2(CO)_9$ is a common product in the reaction of iron carbonyls with sulphur compounds.[9–11]

Reaction of  $(O\quad N)_2S$ *with* $Fe_2(CO)_9$

Reaction of diiron nonacarbonyl with N,N′-thiobismorpholine in THF at room temperature proceeds smoothly according to



$$(O\quad N)_2S + Fe_2(CO)_9 \longrightarrow Fe(CO)_4S(N\quad O)_2 + Fe(CO)_5.$$

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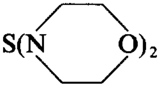
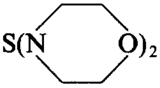
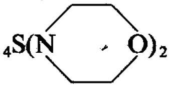
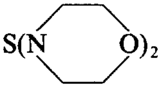
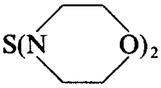
The tetracarbonyliron (N,N′-thiobismorpholine) complex is a brown–orange solid, unstable to air. The compound was fully characterized by analysis, mass spectrometry as well as by IR, ^{1}H NMR and Mössbauer spectroscopy.

The IR spectrum of the complex $Fe(CO)_4$  $S(N\ \ O)_2$ showed four terminal carbonyl bands with frequency and intensity values similar to those found for $Fe(CO)_4L$ complexes, where L is a sulphur-donor ligand.[12,13] Data for $Fe(CO)_4$  $S(N\ \ O)_2$ and other $Fe(CO)_4L$ complexes are shown in Table 1.

In $Fe(CO)_4L$ complexes the ligand L could occupy an axial or equatorial site of the locally trigonal-bipyramidal geometry at iron. Quantitative group theoretical arguments indicate that axially-substituted $Fe(CO)_4L$ complexes (C_{3v} symmetry) should exhibit three IR-active CO stretching frequencies ($2A_1+E$), while equatorially substituted compounds (C_{2v} symmetry) should exhibit four such bands ($2A_1+B_1+B_2$). However, structural assays based solely on IR data could be misleading because, as pointed out by Darensbourg *et al.*,[14] the *E* mode of axially-substituted $Fe(CO)_4L$ compounds is often split, thus yielding a total of four distinct ν(CO) bands. An X-ray study of $Fe(CO)_4$(1,3-dithiane)[15] shows that the sulphur ligand adopts an axial site in a trigonal-bipyramidal array at iron.

In the complexes $Fe(CO)_4L$, with L = pyridine, pyrazine,[16] triphenylphosphine,[17] trimethylarsine and trimethylstibine,[18] the ligand also occupies an axial position in a trigonal-bipyramidal array. Given the similarity of the ν(CO) IR data of compound $Fe(CO)_4$ $S(N\ \ O)_2$ with those for $Fe(CO)_4$(1,3-dithiane) and the other $Fe(CO)_4L$ compounds of known structure, it is reasonable to assume the persistence of the C_{3v} skeletal geometry in the N,N′-thiobismorpholine complex.

The $\nu(S—N)_{as}$ band which in the free ligand is observed at 950 cm^{-1},[19] is lowered to 940 cm^{-1} in the complex by coordination effects. Similar ν(N—S) shifts are observed in the $M(CO)_5$  $S(N\ \ O)_2$ complexes.[6]

The ^{1}H NMR spectra of the complex $Fe(CO)_4$  $S(N\ \ O)_2$ shows the expected signals slightly shifted downfield due to the coordination.

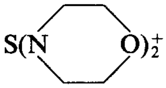
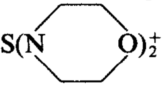
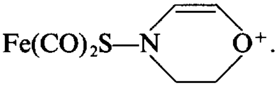
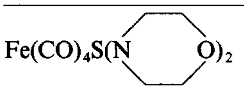
Mass spectral data provide support for the structure of the complex $Fe(CO)_4$ $S(N\ \ O)_2$. The *m/z* fragments corresponding to the molecular ion, ions showing successive loss of CO,  $S(N\ \ O)_2^+$, as well as other fragments expected from the proposed structure, are observed. An interesting feature of the spectrum of the tetracarbonyl(thiobismorpholine)iron complex is the apparent loss of morpholine from the fragment $Fe(CO)_2$ $S(N\ \ O)_2^+$ to give an intense ion of *m/z* 232 and formulated as  $Fe(CO)_2S—N\ \ O^+$.

Table 1. IR spectra of axially-substituted $LFe(CO)_4$ complexes

Complex	ν(CO)^a cm^{-1} (*n*-hexane) $A_1^{(2)}$	$A_1^{(1)}$	*E*		Reference
 $Fe(CO)_4S(N\ \ O)_2$	2050(5.3)	1972(8.6)	1948(9.6)	1935(10)	This work
$Fe(CO)_4$(1,3-dithiane)	2056(7.7)	1981(7.1)	1954(10)	1943(9.7)	12
$Fe(CO)_4$(2-Me_3Si-1,3-dithiane)	2054(7.2)	1975(7.0)	1952(10)	1937(9.4)	12
$Fe(CO)_4$(2-Me_3Pb-1,3-dithiane)	2051(6.8)	1974(6.9)	1948(9.0)	1936(10)	12
$Fe(CO)_4$(1,3-dithia-5-cycloheptene)	2056 s	1979 s	1963 vs	1943 vs	13
$Fe(CO)_4PPh_3$	2050(3.5)	1977(2.2)	1945(10)		14
$Fe(CO)_4NC_5H_5$	2042 s	1970 s	1943 vs		16
$Fe(CO)N_2C_4H_4$	2043 s	1975 s	1948 vs		16
$Fe(CO)_4AsPh_3$	2051 s	1977 s	1947 vs		18

[a] Intensities values in parentheses relative to the strongest band as 10, using a per cent transmission scale.

Confirmation of the trigonal-bipyramidal structure of the complex Fe(CO)$_4$S(N O)$_2$ arises from its ^{57}Fe Mössbauer spectrum which is shown in Fig. 1. The spectrum consists of a single quadrupole splitting. The large quadrupole splitting value QS = 3.1 mm s^{-1} is typical of Fe(CO)$_4$L complexes with a trigonal-bipyramidal structure, QS = 2.3–2.9 mm s^{-1}.[20,21] This result discards a binuclear structure of the type Fe$_2$(CO)$_6$L$_2$ for which QS = 0.6–1.4 mm s^{-1}, the other possible product found in the reaction of iron carbonyl with sulphur ligands. The isomer shift value, IS = 0.23 mm s^{-1}, is characteristic of iron(0) carbonyl derivatives.[20,21] The increase in the IS values in going from Fe(CO)$_5$, QS = 2.5mm s^{-1}, to Fe(CO)$_4$ S(N O)$_2$ can be interpreted as a descrease in the σ-donor ability of N,N″-thiobismorpholine with respect to carbon monoxide. This is consistent with the weak nucleophilic character of N,N′-thiobisamines concluded from the IR[22] and structural data studied.[23] The highest value of the QS parameter for the Fe(CO)$_4$S(N O)$_2$ complex compared with those of (Me$_3$N)$_3$PFe(CO)$_4$, QS = 2.22, PPh$_3$Fe(CO)$_4$, QS = 2.44, Ph$_3$SbFe(CO)$_4$, QS = 2.63, Ph$_3$AsFe(CO)$_4$, QS = 2.68 and (o-Me C$_6$H$_4$)$_3$AsFe(CO)$_4$, QS = 2.93 mm s^{-1},[20] indicates a weaker π-acceptor ability than the phosphine, arsine and stilbine ligands. This agrees with the weak π-acceptor ability of N,N′-thiobisamines suggested from IR data of the M(CO)$_5$S(NR$_2$)$_2$ complexes.[6] We also find that the IS and QS values for the complex Fe(CO)$_4$S(N O)$_2$ occur in the poor π-acceptor region of the Collins–Pettit graph.[24]

Stability of the Fe(CO)$_4$S(N O)$_2$ *complex*

Similar to other Fe(CO)$_4$L complexes where L = sulphur-donor ligand,[13] the complex Fe(CO)$_4$ S(N O)$_2$ is very unstable. Mass and Mössbauer spectroscopic data indicate that this complex decomposes on standing to a mixture of Fe$_3$S$_2$(CO)$_9$[8] and S(N O)$_2$. The difficulty of preparing Fe(CO)$_4$L complexes with L = nitrogen-donor ligand has been mentioned previously.[16] On the other hand, few examples of tetracarbonyl iron complexes with sulphur-donor ligands are known.[12–15] Hence the synthesis of the tetracarbonyl(thiobismorpholine)iron complex is relevant from the point of view of Fe—S compounds as well as from the coordination properties of S—N compounds

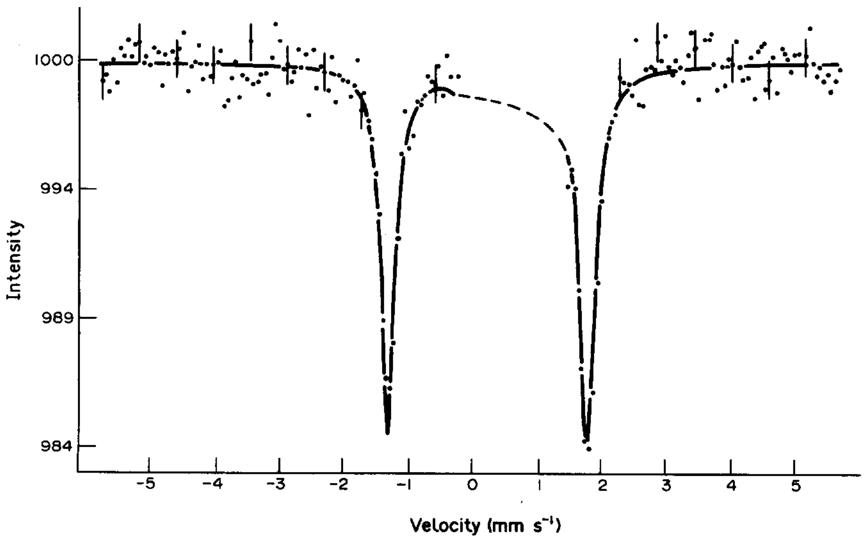
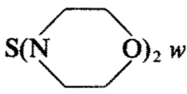
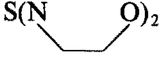


Fig. 1. The Mössbauer spectrum of Fe(CO)$_4$S(N O)$_2$. A small absorption (– – – –) due to decomposition of the sample was subtracted (see text).

Reaction of  $\mathrm{S(N\quad O)_2}$ *with* $Fe_3(CO)_{11}$

From the reaction of triiron dodecacarbonyl with thiobismorpholine in THF at 60°C, unchanged thiobismorpholine and a dark brown solid material were obtained. NMR spectroscopic examination of this product revealed the presence of thiobismorpholine and an unidentified carbonyl species. IR bands in the range 3600–3200 and at 2350 and 800 cm^{-1} [3] also suggest some S—N bond cleavage of the ligand.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$ *with*  $\mathrm{S(N\quad O)_2}$

From the reaction of (dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron tetrafluoroborate[25] with thiobismorpholine a brown solid was isolated. Cleavage of the S—N linkage of the ligand is indicated by their IR spectrum which shows, among others, bands at 3410, 3290, 2040 and 1565 cm^{-1} typical of  $\mathrm{[O\quad NH_2]X}$ salts.[3] Similar behaviour leading to S—N cleavage has been reported in reactions of N,N′-thiobisamines with H$^+$ and with copper(II) salts.[2,3] Hence the S—N bond fission of thiobismorpholine in the presence of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2THF^+$ cation, which is known to act as a Lewis organometallic acid,[26] is no surprise.

EXPERIMENTAL

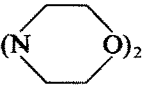
Materials and general procedures

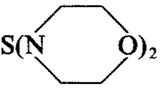
N,N′-thiobismorpholine[1] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$[25] were prepared according to literature methods. The iron carbonyls $Fe(CO)_5$ (Alfa), $Fe_2(CO)_9$ (Fluka) and $Fe_3(CO)_{11}$ (Fluka) were procured commercially and used without subsequent purifications. All solvents were carefully dried prior to use. All operations were performed under an inert atmosphere. Photochemical irradiation was carried out using a UV lamp, Hanau medium pressure, 150 W and a standard irradiation cell.

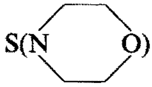
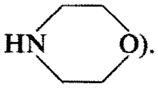
Spectroscopic measurements

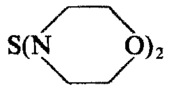
IR spectra were obtained on a Perkin–Elmer 621 instrument. ^{1}H NMR spectra were measured on Varian T-60 apparatus. The mass spectra were determined on a Varian MAT 711 mass spectrometer at an ionizing voltage of 70 eV. The Mössbauer spectrum was determined using a constant acceleration drive system and the data were collected on a Canberra multichannel analyser. The source was ^{57}Co diffused in palladium and sodium nitroprusside was used as standard.

Reaction of  $\mathrm{S(N\quad O)_2}$ *with* $Fe(CO)_5$

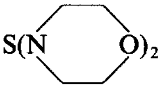
$Fe(CO)_5$ (4.37 g, 22.3 mmol) and  $\mathrm{S(N\quad O)_2}$ (1.8 g, 8.8 mmol) in CH_3OH were irradiated for 3 h at room temperature. The solvent was then removed *in vacuo* and the residue chromatographed on a Florisil column and eluted with *n*-hexane. The resulting red solution was cooled to −20°C overnight to give dark red needles (0.5 g, 25% yield), m.p. 113–114°C (Refs 8, 9, 114°C). Found: C, 22.4. Calc. C, 22.3%. IR (*n*-hexane) 2060, 2045, 2024, 1985 cm^{-1}. Mass spectrum *m/z* 484 (M$^+$ 5%), 456 (M−CO) 428 (M−2CO) 400 (M−3CO), 372 (M−4CO), 344 (M−5CO) 316 (M−6CO), 288 (M−7CO), 260 (M−8CO) 232 (M−9CO), 176 (M−9CO−Fe), 144 (M−9CO−Fe−S).

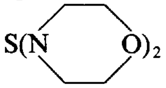
Synthesis of $Fe(CO)_4$ $\mathrm{S(N\quad O)_2}$

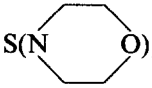
To $Fe(CO)_9$ (2.12 g, 5.82 mmol) was added a solution of  $\mathrm{S(N\quad O)_2}$ (1.1 g, 5.4 mmol) in 50 cm^3 of THF. The mixture was stirred under a static argon atmosphere for 14 h and then solvent and $Fe(CO)_5$ were removed at room temperature *in vacuo*. The residue was extracted with *n*-hexane and after filtration the red–brown solution was cooled to −30°C overnight to give brown–orange solid (0.6 g, 30% yield), m.p. 69–70°C. Found: C, 38.9; H, 4.7; N, 7.9. Calc. for $C_{12}H_{16}O_6N_2SFe$: C, 38.7; H, 4.3; N, 7.5%. IR (*n*-hexane) 2050(s), 1972(s), 1948(vs), 1935(vs) cm^{-1}. NMR ($CDCl_3$) 3.66 (m, 4H, CH_2O), 3.33 ppm (m, 4H, CH_2N). Mass spectrum *m/z* 373 (M$^+$), 345 (M−CO), 316 (M−2CO), 232 (M−2CO− $\mathrm{HN\quad O}$) 176 (M−4CO− $\mathrm{HN\quad O}$).

Attempted reaction of $Fe_3(CO)_{11}$ *with*  $\mathrm{S(N\quad O)_2}$

A solution of $Fe_3(CO)_{11}$ (1.15 g, 2.28 mmol) and

 $S(N\quad O)_2$ (0.60 g, 2.93 mmol) in THF were stirred at 60°C for 2 h, during which it assumed a red–brown colour. The solvent was removed under reduced pressure. The residue was dissolved in *n*-hexane and the solution filtered through Kieselguhr and cooled to -30°C overnight to give brownish-coloured crystals identified by IR and ^{1}H NMR as unreacted N,N′-thiobismorpholine (0.11 g). Following this the solution was evaporated to dryness to give a dark brown oil which solidified on standing. NMR ($CDCl_3$) 3.7 (m, 8H, OCH_2), 3.3 ppm (m, 8H, NCH_2). IR 3600–3200 (m, br), 3000 (m), 2350 (w), 2100–1850 (vs, br), 1600–1400 (m, br), 1260 (s), 1100 (vs), 1060 (vs), 1020 (vs), 920 (m), 800 (s).

Attempted reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2THF]BF_4$ *with*  $S(N\quad O)_2$

To a solution of $[(\eta^5\text{-}C_5H_5Fe(CO)_2THF]BF_4$[25] in CH_2Cl_2 (prepared from $\eta^5\text{-}C_5H_5Fe(CO)_2I$ and $AgBF_4$), was added  $S(N\quad O)_2$ (1.1 g, 5.38 mmol) and stirred for 1 h. The reaction mixture changed from a red to brown–red colour. The resulting solution was evaporated *in vacuo* to dryness, and the solid redissolved in a mixture of *n*-hexane–CH_2Cl_2, filtered and cooled at -30°C. The brown solid residue was dried *in vacuo*. Found: C, 31.7; H, 4.1; N, 4.2. NMR $[(CD_3)_2CO]$ 5.46 (s, 5M, C_5H_5), 3.91 (m, 6H), 3.43 (m, 10H). IR (KBr) 3410 (m), 3290 (m), 2420 (w), 2040 (vs), 1990 (vs), 1565 (m), 1430 (m), 1310 (m), 1150–1000 (vs, br), 905 (m), 890 (m), 880 (m), 873 (s), 610 (m, br).

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