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Iron(II) thiolates as reversible carbon monoxide carriers

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Abstract

Solutions of several iron(II) thiolato complexes in methanol, dimethylformamide or 2-ethoxyethanol reversibly absorb and release carbon monoxide at atmospheric pressure and 20–50 °C. Solutions of $Fe(SPh)_2(H_2NCH_2CH_2NH_2)(CO)_2$ and of an anionic complex tentatively formulated as $[Fe_2(SPh)_5(CO)_4]^-$ in 2-ethoxyethanol and of Fe(L-$SCH_2CH(NH_2)COOEt)_2(CO)_2$ in dimethylformamide were found to be most effective for the separation of CO–N_2 gas mixtures.

Introduction

Solutions of Fe^{2+} and thiols readily absorb carbon monoxide in the presence of bases and additional ligands containing S, N or P donor atoms forming carbonyl derivatives of iron(II) thiolates [1–9]. Recently some of us reported the preparation of the anionic iron(II) complex $[Fe(SPh)_3(CO)_3]^-$ which contains only thiolato ligands and is formed from Fe^{2+} and excess PhS^- by absorption of CO [10].

Many of these complexes are quite stable but some of them easily lose the CO ligands. Thus, Fe(L-$SCH_2CH(NH_2)COOH)_2(CO)_2$ is decarbonylated upon irradiation with visible light [11] and the dithiophosphate complexes $Fe[S_2P(OR)_2](CO)$ – which can be prepared from $FeI_2(CO)_4$ and $(RO)_2PS_2K$ – are not sufficiently stable against CO loss at room temperature to be isolated in solid form [5]. These observations prompted us to investigate some Fe^{2+}–thiolate systems as to their suitability as reversible carbon monoxide carriers. The reversible uptake of carbon monoxide by FeN_4 type complexes or iron(II) with bi- or tetradentate nitrogen donor ligands has already been studied [12–14].

Experimental

Measurement of CO absorption

The starting iron compound ($FeSO_4 \cdot 7H_2O$ when methanol, or $FeCl_3$ when dimethylformamide or 2-ethoxyethanol were used as solvents) and a part of the solvent were measured into a Schlenk tube equipped with a magnetic stirrer, a dropping funnel and connected to a gas burette. The thiol and the equivalent amount of base (NaOMe or an amine) dissolved in the other part of the solvent were put into the dropping funnel and the system secured and filled with CO. The temperature of the apparatus was adjusted to 20 °C with a thermostat and the content of the dropping funnel added to the iron containing solution under constant stirring. The volume of CO absorbed was measured with the gas burette.

Reversibility of carbon monoxide absorption and desorption

The repeated absorption and desorption of CO was investigated in the continuously operated glass apparatus shown in Fig. 1; details of the absorber and desorber vessels can be seen in Fig. 2.

The solution (250 ml) containing the desired iron carbonyl complex was prepared separately by reacting $FeSO_4 \cdot 7H_2O$ or $FeCl_3$ (12 mmol), the thiol, and the necessary base (NaOMe, Et_3N or ethylenediamine) dissolved in the solvent with CO under atmospheric pressure. Absorber (1), desorber (2), the heat exchangers (3) and the connecting tubes were filled up with this solution, their temperature adjusted with thermostats (8) to the desired value(s) and the circulation of the liquid started with a peristaltic pump (4). A CO:N_2 = 1:1 gas mixture was bubbled into the absorber (1) and H_2 was bubbled into the desorber (2) through fritted glass and the contact between gas and liquid phases further intensified by magnetic stirrers (6). Gas bubbles eventually entrained in the liquid were sep-

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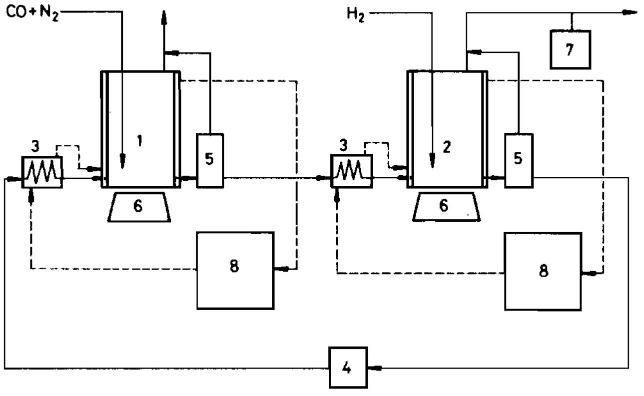

Fig. 1. Continuous absorber–desorber apparatus: 1, absorber; 2, desorber; 3, heat exchangers; 4, peristaltic pump; 5, gas–liquid separator; 6, magnetic stirrer; 7, gas chromatograph; 8, thermostat.

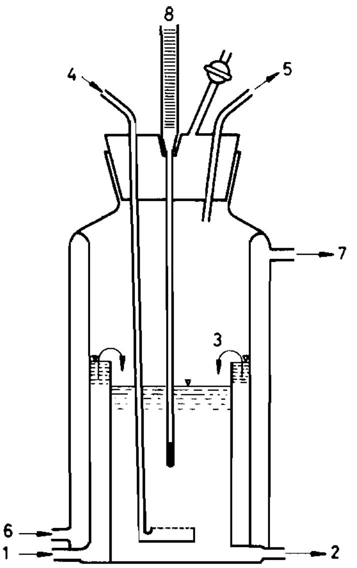

Fig. 2. Details of absorber and desorber vessel: 1, complex solution inlet; 2, complex solution outlet; 3, direction of liquid flow; 4, gas inlet; 5, gas outlet; 6, thermostatting liquid inlet; 7, thermostatting liquid outlet; 8, thermometer.

arated in separators (5) and the CO and N_2 content of the H_2 leaving desorber (2) was periodically determined with a gas chromatograph (7). The increase of the $CO:N_2$ ratio above 1:1 in the desorbed gas indicated the CO carrier capacity of the iron complexes in the investigated solution, and the amount of liquid circulated through the two reaction vessels during the whole experiment defined the number of reversible absorption–desorption cycles achieved with these complexes.

Results and discussion

Three types of iron(II) thiolates were investigated in detail with regard to their capacity as reversible carbon monoxide carriers: (a) the complex $Fe(SPh)_2(H_2NCH_2CH_2NH_2)(CO)_2$ [9], (b) the complex $Fe(L\text{-}SCH_2CH(NH_2)COOEt)_2(CO)_2$ [9] and (c) the anionic iron complexes containing only thiolato and carbonyl ligands which were formed in the absence of chelating ligands when the thiolates were present in excess. One representative of such complexes, the anion $[Fe(SPh)_3(CO)_3]^-$ has already been isolated in the form of its Na(15-crown-5) and K(18-crown-6) salts from THF solutions [10]; IR spectra showed, however, that in those solvents which were used in this work mainly other, upto now not described, iron carbonyls were formed. Despite numerous experiments we did not succeed in isolating these complexes in a pure state. Since, however, according to our experiments they played a dominant role in the reversible uptake and release of CO, we made efforts to determine their probable composition from other observations and to suggest a plausible formula for these substances.

Measurement of CO absorption and identification of carbonyl complexes

Screening several variables to find the most suitable systems, absorption of carbon monoxide by Fe^{2+} or Fe^{3+} solutions was measured in methanol, 2-ethoxyethanol or dimethylformamide solvents in the presence of the following thiols, aminothiols and amines:

- ethanethiol, 2-butanethiol, 1-octanethiol, tert-butanethiol, benzyl mercaptan, thiophenol, *p*-methoxythiophenol, *p*-chlorothiophenol
- L-cysteine, L-cysteine ethyl ester, *N*-acetyl-L-cysteine, cysteamine, penicillamine, *o*-aminothiophenol
- triethylamine, diethylamine, ethylenediamine, *o*-phenylenediamine

The experimental results allow the following conclusions:

(1) Carbon monoxide absorption never exceeded 2 mol for 1 mol of iron. In the case of aminothiols like L-cysteine ethyl ester, or *o*-aminothiophenol and with the ligand combination thiophenol plus ethylenediamine this is in complete accord with the expected formation of complexes like $Fe(L\text{-}SCH_2CH(NH_2)COOEt)_2(CO)_2$ and $Fe(SPh)_2(H_2NCH_2CH_2NH_2)(CO)_2$ which have been described earlier [9].

This result was, however, somewhat unexpected in those cases where only thiols (and the necessary amount of base) were added to the iron containing solutions because the formation of $[Fe(SPh)_3(CO)_3]^-$ or its analogues would have required the absorption of 3 mol of CO. The upper limit (2 mol) of CO absorption was, however, usually only attained in methanol as solvent; in 2-ethoxyethanol and dimethylformamide CO absorption had in many cases already stopped at lower levels (0.6–1.8 mol CO/mol Fe). The latter phenomenon may be either the result of a competition between the solvent and CO for coordination sites or may be of kinetic character. Our reversibility experiments in these two solvents which will be discussed in the next paragraph support thermodynamic (equilibrium) factors in the case of PhSH and kinetic factors in the case of EtSH as ligands. No CO uptake could be observed with tert-butanethiol.

(2) Irrespective of whether $FeSO_4 \cdot 7H_2O$ or $FeCl_3$ was used as starting iron compound the same iron carbonyl thiolates were always formed as shown by the IR spectra. The only difference between the two iron compounds was that $FeCl_3$ required 1 mol of excess thiol which was necessary to reduce Fe(III) to Fe(II). This can be seen from Table 1 which shows the absorption of CO by solutions of $FeSO_4 \cdot 7H_2O$ or $FeCl_3$, thiophenol and NaOMe in methanol at different Fe:PhS^- ratios. Because of solubility, $FeSO_4 \cdot 7H_2O$ was usually used in experiments with methanol, and $FeCl_3$ with 2-ethoxyethanol or dimethylformamide as solvents.

(3) The IR spectra of the solutions obtained after CO absorption showed, as expected, the formation of $Fe(L\text{-}SCH_2CH(NH_2)COOEt)_2(CO)_2$ or $Fe(SPh)_2(H_2NCH_2CH_2NH_2)(CO)_2$ [9] in the experiments with L-cysteine ethyl ester or thiophenol and ethylenediamine. If only thiols and an equivalent amount of base were used at least three absorption bands always appeared showing the following pattern: a very strong band around 2000–2010 cm^{-1}, a weak band (in many cases only as a shoulder) approximately 10 wavenumbers higher, and a band of medium intensity between 1930–1970 cm^{-1}. These three bands apparently belonged to the same type of complex, the positions of the absorption bands being influenced only by the solvent and the electron acceptor/donor properties of the thiolato ligands. In the case of thiophenol two additional weak bands could be observed at 2052 and 1993 cm^{-1} (the latter one as a shoulder). Representative results are compiled in Table 2.

Additional information, which can be seen from Table 2 is that only in the case of thiophenol (and of substituted thiophenols, not shown in the Table) was ethylenediamine incorporated into the iron carbonyl complexes formed under such conditions. Aliphatic thiols like ethanethiol or benzylthiol formed the same complexes irrespective of whether ethylendiamine was present or not. This observation suggests that the tendency for formation of the new 'three-band complexes' containing only thiolato ligands is especially strong for aliphatic thiols. Such a conclusion is also supported by our absorption/desorption experiments discussed in the next paragraph.

TABLE 1. Absorption of CO by methanol solutions of $FeSO_4 \cdot 7H_2O$ (or $FeCl_3$), thiophenol and NaOMe

Mole ratio		Absorbed CO (mol/mol Fe)	
PhS^-/Fe	NaOMe/Fe	with $FeSO_4 \cdot 7H_2O$	with $FeCl_3$
1.0	1.05	0.66	
1.5	1.6	1.01	
2.0	2.1	1.34	0.63
2.5	2.6	1.70	
3.0	3.1	2.00	1.33
4.0	4.2	2.04	2.00
5.0	5.2	2.03	1.98

TABLE 2. IR spectra in different solvents obtained after CO absorption

Thiol	N-ligand	ν(C–O) (cm^{-1})		
		MeOH	DMF	2-ethoxy-ethanol
PhSH		2060w 2020m, sh 2013vs 1969s		2052w 2015m, sh 2006vs 1993m, sh 1963s
PhSH	ethylene-diamine	2026vs 1972vs	2014vs 1958vs	2021vs 1966vs
EtSH		2009m 1997vs 1949s	1997m 1983vs 1933s	2002m, sh 1988vs 1941s
EtSH	ethylene-diamine	2009m 1997vs 1950s	1996m 1982vs 1931s	2003m, sh 1988vs 1941s
$PhCH_2SH$		2012m, sh 2000vs 1954s	2003w 1989vs 1940s	2007m, sh 1994vs 1946s
L-Cysteine ester	ethyl	2025vs 1968vs	2013vs 1951vs	2016vs 1956vs

Starting iron compound $FeSO_4 \cdot 7H_2O$ in methanol or $FeCl_3$ in dimethylformamide and 2-ethoxyethanol; 1 mmol in 100 ml solvent. RSH:ethylenediamine:Fe = 3:0:1 or 2:1:1 in methanol and 4:0:1 or 3:1:0 in dimethylformamide or 2-ethoxyethanol. L-Cysteine ethyl ester:Fe = 2:1 in methanol and 3:1 in dimethylformamide or 2-ethoxyethanol. RSH:base (NaOMe or Et_3N) = 1:1.

It should be mentioned here that the results were always the same whether NaOMe or Et_3N (or eventually another primary amine) was used as a base. Monoamines were apparently not incorporated into any of the complexes formed.

We suggest that the new 'three-band complexes' formed from thiolates, Fe^{2+} (or Fe^{3+}) and CO are dinuclear complexes of the overall formula $[Fe_2(SR)_5(CO)_4]^-$ and the structure $[(CO)_2(PhS)Fe(\mu\text{-}SPh)_3Fe(SPh)(CO)_2]^-$. We support our suggestion with the following experimental facts.

(a) 2 mol of CO are absorbed for 1 mol or iron.

(b) The relatively low wavenumbers of the ν(C–O) bands are compatible with an anionic character of the complex.

(c) The intensities of the additional weak bands observed in the case of thiophenol, at 2052 and 1993 cm^{-1} in 2-ethoxyethanol and at 2060 cm^{-1} in methanol increased on increasing the PHS^-:Fe ratio. Since these two bands belong to the known $[Fe(SPh)_3(CO)_3]^-$ anion [10] this proves that the equilibrium between the two complexes is shifted by an increase in the RS^-:Fe ratio towards the mononuclear species and therefore the RS^-:Fe ratio in the 'three-band complex' has to be smaller than 3:1.

(d) The solutions containing these types of complexes are dark brown which is in strong contrast to the vivid light red color of the $[Fe(SPh)_3(CO)_3]^-$ anion. Darker colors usually point to higher nuclearity metal carbonyls.

(e) In order to further support the lower than 3:1 ratio of sulfur to iron in these complexes we reinvestigated the preparative method described [10] for $[Fe(SPh)_3(CO)_3]^-$ from $Fe_3(SPh)_6(CO)_6$, NaSPh and CO in THF. In a series of experiments the NaSPh:$Fe_3(SPh)_6(CO)_6$ ratio was systematically increased from 1:1 to 4:1 (the ratio given in the preparative method) and the resulting solutions investigated by IR spectroscopy. The spectra unambiguously showed that at lower ratios both $[Fe(SPh)_3(CO)_3]^-$ and $[Fe_2(SPh)_5(CO)_4]^-$ were formed, but on increasing the PhS^-:Fe ratio the concentration of the dinuclear complex went through a maximum then gradually decreased and at the molar ratio of 4:1 a complete transformation into the mononuclear complex was obtained.

Reversibility of carbon monoxide absorption and desorption

Table 3 summarizes our results obtained in the continuous experiments performed in the apparatus shown in Fig. 1. Liquid and gas flow rates were 0.5 mol/s iron carbonyl solution, 1.73 ml/s $CO+N_2$ gas mixture on the absorber side, and 0.66 ml/s H_2 on the desorber side. Preliminary experiments have shown that these values gave the best results under our experimental conditions.

The CO/N_2 ratio in the desorbed gas reached its highest value shortly after attaining steady state conditions and gradually decreased afterwards due to a slow deterioration of the circulating iron carbonyl solution. The rate of this deterioration process varied videly, some solvent–ligand combinations were much more resistant than others. Table 4 shows two typical examples: the thiophenol containing complex in 2-ethoxyethanol (which proved to be the most resistant in our experiments) and the cysteine ethyl ester complex in dimethylformamide. The chemistry of this deterioration process was not investigated, one reason may have been the diffusion of oxygen through the rubber tubings into the apparatus. As shown by the significant differences between the systems investigated, however, other chemical transformations were also responsible. Table 3 always shows the highest observed value of this ratio.

The number of cycles shown in Table 3 was calculated by dividing the total volume of liquid recirculated through the system by the amount of solution present in the apparatus (250 ml) thus defining how many times (on the average) each iron complex was forced to take up or to release its CO ligands. This number obviously depended therefore on how long each experiment was run. The experiments were usually stopped when the difference between the increased CO/N_2 ratio and the CO/N_2 ratio of the blank experiments (in which the

TABLE 3. Separation of $CO–N_2$ gas mixtures in continuous absorption/desorption experiments

S (and N) containing ligand	Temperature of desorber (°C)	CO/N_2 ratio in desorbed gas			No. adsorption/desorption cycles		
		Methanol	Dimethylformamide	2-Ethoxyethanol	Methanol	Dimethylformamide	2-Ethoxyethanol
	20	0.98	1.00	0.90			
	50			1.03			
Thiophenol	20	4.41		5.72	45		70
	50			12.0			96
Thiophenol + ethylenediamine	20	2.00	2.00[a]	3.43	38	7	45
	50			6.16[a]			20
Benzyl mercaptan	20	0.78[a]	0.73				
	50		4.31	2.49		40	22
Ethanethiol	20	0.85	0.75				
	50			1.57[a]			9
Cysteine ethyl ester	20	0.94[a]	1.55		10	71	
	50		7.32			39	

12 mmol iron compound in 250 ml solvent. For other reaction conditions see Table 2. [a]Precipitate formation.

TABLE 4. Change of the CO/N_2 ratio with time within one continuous adsorption–desorption experiment

Experiment no.	Time	No. adsorption–desorption cycles	CO/N_2 ratio of desorbed gas
1[a]	20 min	2.3	11.5
	1 h	7	9.3
	2 h	14	12.0
	3 h	21	11.9
	5 h	34	11.8
	10 h	69	11.5
	11 h	76	10.1
	14 h	96	7.51
2[b]	20 min	2.1	7.32
	1 h	6.5	7.10
	2 h	13	7.08
	3 h	19	6.91
	4 h	26	6.17
	5 h	32	4.95
	6 h	39	3.85

[a]Ligand thiophenol, solvent 2-ethoxyethanol. [b]Ligand L-cysteine ethyl ester, solvent dimethylformamide. Temperature of desorber in both cases 50 °C.

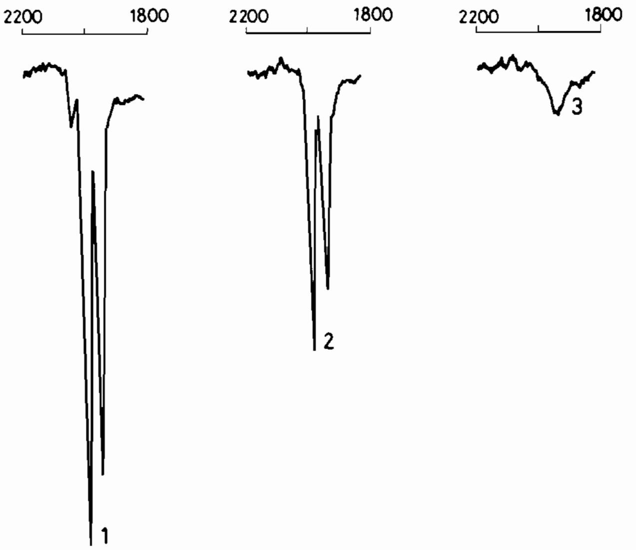

Fig. 3. IR spectra of liquid samples taken from the continuous apparatus: 1, starting solution; 2, sample from the absorber under steady state conditions; 3, sample from the desorber under steady state conditions.

solutions contained no CO transporting complexes) dropped to about one half of its highest observed value.

As can be seen from the results, three systems gave the best results with regard to both CO enrichment and durability: two of these contain thiophenol (and the corresponding amount of Et_3N or ethylenediamine) in 2-ethoxyethanol, and the third L-cysteine ethyl ester (and an equivalent amount of Et_3N) in dimethylformamide. The complexes formed from benzyl mercaptan performed less well, and the absorption of CO by ethanethiol complexes of Fe(II) proved to be practically irreversible under our conditions.

As expected, an increase of the desorber temperature from 20 to 50 °C improved the enrichment factors. Under such conditions the solution leaving the desorber practically did not contain any carbonyl complex, as shown by the IR spectra. This can be seen from Fig. 3 which shows the IR spectra in the 2200–1800 cm^{-1} region of the starting solution (prepared in 2-ethoxyethanol from $FeCl_3$, PhSH and Et_3N under CO) and of the same solution leaving the absorber and the desorber during the experiment under steady state conditions. These spectra suggest that a further improvement in CO enrichment could be achieved by improving the conditions for the absorption step because the concentration of carbonyl complexes in the latter is too far from the theoretical maximum defined by the starting composition. The most plausible way to achieve this would be to increase the volume of the absorber in order to increase the residence time of the solution in this part of the apparatus.

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References

1 M. P. Schubert, *J. Am. Chem. Soc., 55* (1933) 4563.
2 K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc., 98* (1976) 6951.
3 D. Sellmann, P. Kreutzer and E. Unger, *Z. Naturforsch., Teil B, 33* (1978) 190.
4 D. Sellmann, H. E. Jonk, H. R. Pfeil and J. V. Seyerl, *J. Organomet. Chem., 191* (1980) 171.
5 J. Takács and L. Markó, *Transition Met. Chem., 9* (1984) 10.
6 D. Sellmann, U. Kleine-Kleffmann, Z. Zapf, G. Huttner and L. Zsolnai, *J. Organomet. Chem., 263* (1984) 321.
7 D. Sellmann, G. Freyberger, R. Eberlein, E. Böhlen, G. Huttner and L. Zsolnai, *J. Organomet. Chem., 323* (1987) 21.
8 J. Takács, L. Markó and L. Párkányi, *J. Organomet. Chem., 361* (1989) 109.
9 J. Takács, E. Soós, Z. Nagy-Magos, L. Markó, G. Gervasio and T. Hoffmann, *Inorg. Chim. Acta, 166* (1989) 39.
10 Z. Nagy-Magos, L. Markó, A. Szakács-Schmidt, G. Gervasio, E. Belluso and S. F. Kettle, *Bull. Soc. Chim. Belg., 100* (1991) 445.
11 A. Tomita, H. Hirai and S. Makishima, *Inorg. Chem., 6* (1967) 1746.
12 L. Vaska and T. Yamaji, *J. Am. Chem. Soc., 93* (1971) 6673.
13 B. B. Wayland, L. F. Mehne and J. Swartz, *J. Am. Chem. Soc., 100* (1978) 2379.
14 C. A. Koval, R. D. Noble, J. D. Way, B. Louie, Z. E. Reyes, B. R. Bateman, G. M. Horn and D. L. Reed, *Inorg. Chem., 24* (1985) 1147.