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MIXED IRON COBALT CARBONYL SULPHIDES *

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Summary

Two new mixed iron cobalt carbonyl sulphide clusters $HFe_2Co(CO)_9S$ and $Fe_2Co(CO)_8(NO)S$ have been prepared and characterized. The hydride complex undergoes acidic dissociation in polar solvents and the resulting anion was isolated as $(Et_4N)[Fe_2Co(CO)_9S]$. An efficient high pressure synthesis has been found for $H_2Fe_3(CO)_9S$.

Introduction

The first mixed metal carbonyl sulphide, $FeCo_2(CO)_9S$ (I) was described several years ago [1]. More recently the isoelectronic iron carbonyl cluster $H_2Fe_3(CO)_9S$ (II) was prepared [2], and this suggested that it should be possible to make similar compounds containing the Fe_2CoS core. This paper describes such syntheses.

Results and discussion

Cluster II can be prepared by the acidification of a basic methanol solution containing the $HFe(CO)_4^-$ anion and sodium sulphide in a 3/1 molar ratio of iron to sulphur [2]. We find that the acidification of a similar solution which contain also the $Co(CO)_4^-$ anion in the presence of hexane leads to $Co_3(CO)_9S$, I, and II (the relative amounts of those complexes depending on the Fe/Co ratio), minor amounts of $Fe_2(CO)_6S_2$, $Fe_3(CO)_9S_2$ and $Fe_3(CO)_{12}$, and a new compound which was identified as $HFe_2Co(CO)_9S$ (III). The Fe_2Co compound was separated from the other complexes by repeated chromatography of the hexane solution on a silica gel column, but the yields were rather low because of the very small difference between the retention characteristics of the Fe_2Co and $FeCo_2$ complexes. Thus an alternative method of preparation was developed by applying the principle of redox condensation [3] which was successfully used for the synthesis of two other mixed iron cobalt carbonyl clusters

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* Dedicated to the memory of Professor Paolo Chini.

$HFeCo_3(CO)_{12}$ [4] and (PPN)[$CoFe_3(CO)_{13}$] [5]. In our case the reaction between $Fe_3(CO)_9S^{2-}$ [2] and $Co_2(CO)_8$ in dichloromethane as solvent proved to be a practical way of obtaining the $Fe_2Co(CO)_9S^-$ anion

$$Fe_3(CO)_9S^{2-} + Co_2(CO)_8 \xrightarrow{CH_2Cl_2} Fe_2Co(CO)_9S^- + Co(CO)_4^-$$

(+ minor amounts of $Fe(CO)_5$)

Acidification yielded the desired III free of I, and so III was easily obtained pure in reasonable yields (15—30% based on II) by chromatography on silica gel.

An even more efficient method for the preparation of III involved a modification of the recently improved synthesis of I [6], which is based on the stability of the $Fe_2Co(CO)_9S^-$ anion. Using Na_2S or NaSEt as sulphur source (instead of EtSH which leads to I) and working in a polar solvent under CO pressure at 150°C, mixtures of $Fe(CO)_5$ and $Co_2(CO)_8$ give a solution of Na^+ $Fe_2Co(CO)_9S^-$ from which I can be isolated after acidification in 50—77% yield based on the starting carbonyls. In the absence of $Co_2(CO)_8$ the $HFe_3(CO)_9S^-$ anion is formed under the same conditions, and this provides a useful new way for the preparation of II in high yield (38—82%). These results are listed in Table 1. Apparently all $Fe_nCo_{3-n}(CO)_9S$ clusters show a higher tendency to form under CO pressure at higher temperatures [6].

III forms hexane soluble violet crystals and is diamagnetic. Its IR spectrum in the CO stretching region (Table 2) is very similar to that of I indicating an analogous structure (see Fig. 1). The bridging hydride ligand is responsible for the singlet at δ —20.9 ppm (in $CHCl_3$) in the ^1H NMR spectrum. We were not able to obtain a satisfactory ^{13}C NMR spectrum.

When III is dissolved in polar solvents such as ethanol or acetone it loses its hydride ligand as a proton.

$$HFe_2Co(CO)_9S \xrightarrow{solv} Fe_2Co(CO)_9S^- + solv \cdot H^+$$

This is shown by the change in the infrared spectrum (Table 1) and the isolation of the anion as $(Et_4N)[Fe_2Co(CO)_9S]$. This ionic derivative is very soluble in polar organic solvents, and is difficult to crystallize, but crystals were obtained by the slow diffusion method with a chloroform/cyclohexane solvent system. The IR spectrum shows that the loss of the hydride ligand does not increase the symmetry of the molecule and thus excludes a structure for III in which the H is positioned between the cobalt and one of the iron atoms (a

TABLE 1

SYNTHESIS OF II AND III UNDER HIGH PRESSURE (Temperature 150°C, CO pressure 100 bar at 20°C)

Sulphur compound	Fe/Co/S ratio	Solvent	Product [a] and yield (%)
Na_2S	3/0/1	10% NH_3 in EtOH	II, 82
Na_2S	3/0/1	EtOH	II, 38
Na_2S	2/2/1	EtOH	III, 50
EtSNa	1/1/1	EtOH	III, 77

[a] After acidification.

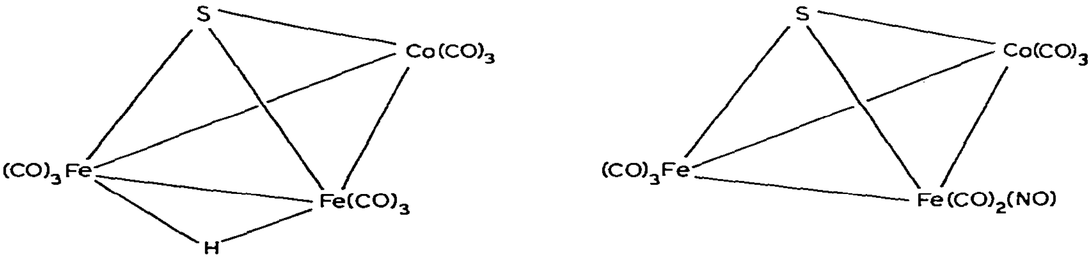
TABLE 2

INFRARED SPECTRA IN THE ν(CO) REGION (cm^{-1})

III (in hexane)	III (in acetone)	IV (in hexane)
2102 w	2055 w	2094.5 m
2061 vs	2002 vs	2060.5 vs
2055 vs	1992 vs	2048.5 s
2031 s	1975.5 s	2046 s
2011 m	1932.5 m	2037 s
2000.5 m	1915 w (sh)	2031 s (sh)
		2025 m (sh)
		2006 w (br)
		2001 w (br)
		1986 m
		1794 s

structure which is also improbable on electron-counting arguments). The shift of 50—60 wavenumbers is in accord with one negative charge for three metal atoms.

If a solution of the $Fe_2Co(CO)_9S^-$ anion is acidified in the presence of sodium nitrite (1 mol per mol of complex) and hexane, $Fe_2Co(CO)_8(NO)S$ (IV) is formed and can be isolated by crystallization from the hexane solution in about 70% yield. The IR spectrum of this diamagnetic red brown compound shows a band at 1794 cm^{-1} (in hexane) or 1778 cm^{-1} (in KBr) which is characteristic for the NO ligand. The rather complex pattern of the ν(CO) bands (the purity of the compound was confirmed by repeated TLC and column chromatography on silica gel) suggests the presence of isomers in hexane solution, but this possibility was not supported by measurements at low temperatures since the IR spectrum did not change noticeably between +20 and —60° C. The mass spectrum of the compound shows the stepwise and random loss of the eight CO and one NO ligands, with a strong molecular ion at 457. In accord with the absence only of a hydride ligand, the IR spectrum of IV in polar solvents is qualitatively similar to that in hexane, only a broadening of the bands being observed.



(III)

(IV)

Fig. 1. Proposed structures of III and IV.

The structures proposed for complexes III and IV (Fig. 1) are further supported by the Mössbauer spectra, recorded at 77 K. Complex III gives only one signal (isomer shift relative to the $^{57}Co/Pt$ source —0.44 mm s^{-1}, quadrupole splitting 0.67 mm s^{-1}) and contains therefore only one type of iron atom. In the case of complex IV two signals appear (isomer shifts —0.36 and —0.42 mm s^{-1}, quadrupole moments 0.85 and 0.72 mm s^{-1}, respectively) corresponding to the two different iron atoms.

According to our knowledge IV is the first heterometallic cluster including a nitrosyl ligand [7] which is a chiral molecule [8].

Experimental

All preparations were performed under Ar.

Preparation of III from II

To a solution of 0.68 g II (1.5 mmol) in 50 ml pyridine was added a solution of 3.3 mmol of $(Et_4N)OH$ in 1.4 ml water. The mixture was evaporated to dryness in vacuo and the residue was dissolved in 100 ml CH_2Cl_2. Then 0.46 g $Co_2(CO)_8$ (1.35 mmol) was added, and the solution was stirred for 5 h, set aside for 3 days, then evaporated to dryness in vacuo. The residue was dissolved in 50 ml methanol and 50 ml hexane, and the solution was acidified with dilute hydrochloric acid. The dark hexane layer was separated and the water layer was extracted three times with 50 ml hexane. The hexane solutions were combined and chromatographed on a silica gel column. The first violet fraction was collected and concentrated in vacuo to about 50 ml then chilled to —78°C to give 180 mg of crystalline III which was filtered off (0.40 mmol, 26% yield based on II). (Found: Fe, 24.6; Co, 13.6; S, 6.9. $C_6HO_9CoFe_2S$ calcd.: Fe, 24.51; Co, 12.92; S, 7.03%.)

High pressure synthesis of III

A mixture of 6.7 mmol $Fe(CO)_5$ (0.89 ml), 3.3 mmol $Co_2(CO)_8$ (1.14 g), and 3.3 mmol $Na_2S \cdot 9\ H_2O$ (0.80 g) and 10 ml ethanol was heated in a 20 ml autoclave at 150°C under CO (starting pressure at 20°C, 100 bar) for 3 h. The resulting dark brown solution was evaporated in vacuo, the residue was dissolved in 20 ml methanol, 10 ml water and 50 ml hexane were added and the mixture was acidified with dilute hydrochloric acid. The hexane layer was separated and the water layer extracted four times with 50 ml hexane. The combined hexane extracts were chilled to —78°C and the violet crystals of III were filtered off. Yield 760 mg (1.67 mmol, 50%).

The high pressure synthesis of II was performed similarly.

Preparation of $(Et_4N)[Fe_2Co(CO)_9S]$

To a solution of 23 mg of III (0.05 mmol) in 2 ml pyridine was added a solution of 0.06 mmol of $(Et_4N)OH$ in 40 μl water. The solution evaporated to dryness in vacuo and the residue dissolved in 6 ml chloroform. The solution was filtered and 5 ml cyclohexane was added as a top layer. During 5 days a few crystals separated. (Found: C, 34.1; H, 3.75; N, 2.7; Fe, 18.7. $C_{17}H_{20}O_9NCoFe_2S$ calcd.: C, 34.90; H, 3.45; N, 2.39; Fe, 19.09%.)

Preparation of IV

To a solution of 228 mg of III (0.5 mmol) in 50 ml methanol was added, a solution of 35 mg $NaNO_2$ (0.5 mmol) and 40 mg NaOH (1 mmol) in 10 ml water. The solution was stirred for a few minutes, then 50 ml hexane were added and the mixture was acidified with dilute hydrochloric acid. The dark hexane layer was separated, dried, and chilled to −78°C. 156 mg of crystalline IV were obtained by filtration (0.34 mmol, 68% yield). (Found: N, 3.1; Fe, 23.6, Co, 12.2; S, 7.1. $C_8O_9NCoFe_2S$ calcd.: N, 3.07; Fe, 24.45; Co, 12.90; S, 7.02%.)

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