Synthesis, Characterization and Reactions of Some Iron-Sulfur Cluster Complexes

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Abstract: Reactions of disodiumtetracarbonylferrate, Na_2 [Fe $(CO)_4$] with Sulfur and SCl_2 respectively in refluxing THF yield the corresponding ferredoxin analouge Fe-S cluster complex, [Fe_4S_4 $(CO)_{12}$] (1) and butterfly complex, [Fe_4S_4 $(CO)_{12}$] (2) having different structures. Substitution reaction of 1 with PPh_3 in refluxing cyclohexane yields [Fe_4S_4 $(CO)_{11}$ (PPh_3)] (3). The complex 2 is found to be unstable in common organic solvents and decomposes to [Fe_3 $(CO)_{12}$]. All complexes have been characterized by IR, ^{1}H NMR and mass spectra.

Key words: Ferredoxin, Butterfly, Fe-S cluster, Substitution, Refluxing, Unstable and Decompose.

Introduction

Transition metal complexes containing single atom ligands derived from certain main groups of the periodic table have evidenced considerable interest in recent times [1-3]. The use of main group elements as ligands firstly serve to stabilize polynuclear metal carbonyl frameworks and secondly act as initial sites of addition in cluster growth reactions. From group 16 of the periodic table, S has been extensively used for stabilization of unusual structures and as sites on which coordinatively unsaturated metal carbonyl groups can add [4-5]. Early work on metal-chalcogenide complexes suggested that while Sulfur and selenium showed similar behavior, the reactivity of tellurium was often unique [6-9]. Recently it has been evidenced that selenium displays some unique reactivity features, in its compounds of iron, towards small organic molecules [10]. The compounds [$(CO)_6$ $Fe_2(\mu\text{-}E_2)$] [E = S, Se, Te] are useful starting materials for addition of organic and inorganic species [11-13]. There is much interest in the synthesis and characterization of metal complexes containing methylene and other alkylidene groups, because these species are known to be intermediates in many catalytic reactions [14-16]

Typically, the reactions of compounds [$(CO)_6Fe_2(\mu\text{-}E_2)$] involve addition across the E-E bond [17,18]. There are the available reports on the chemistry of [$(CO)_6Fe_2(\mu\text{-}S_2)$] but our attempts were to investigate the reactions of $Na_2[Fe(CO)_4]$ with Sulfur and SCl_2 respectively. The main objective was to see the synthesis of Fe-S clusters containing Fe_4S_4 core and study their potential use. In this paper, we describe the synthesis, characterization and reactions of Fe-S clusters [Fe_4S_4 $(CO)_{12}$] and [$Fe_4S_4(CO)_{12}$] having different structures.

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Experimental

All reactions and subsequent work-up were carried out in dry nitrogen atmosphere. THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. Hydrocarbon solvents were dried over sodium wire. $Na_2[Fe(CO)_4]$[19] was prepared according to the published method. $Fe(CO)_5$, PPh_3, S and SCl_2 were used as received. IR spectra were recorded on a Shimadzu 8010 spectrometer, ^{1}H NMR spectra on a Bruker 500 MHz spectrometer and mass spectra on a high resolution mass spectrometer.

Reaction of $Na_2[Fe(CO)_4]$ with Sulfur

To a freshly prepared THF (40 mL) solution of $Na_2[Fe(CO)_4]$ (1.09 g, 5.1mmol) was added a solution of Sulfur (0.16 g, 0.64 mmol) in the same solvent under nitrogen atmosphere with vigorous stirring at refluxing condition. After completion of addition, the reactants were allowed to stir for 6 hours. The course of the reaction was monitored by analytical TLC. The solvent was removed and the residue was extracted with petroleum ether (40-60°C) and diethyl ether mixture (1:1, v/v) and filtered on kieselguhr. The filtrate was concentrated and chromatographed over a column of silica gel (230-400 mesh) and eluted with petroleum ether (40-60°C) to give a red band which on removal of solvent yielded $[Fe_4S_4(CO)_{12}]$ (**1**) as ruby red crystals (0.39 g, 45%, m.p. 84-86°C). IR (cyclohexane, vCO): 2083, 2062, 2042, 2006, 1990, 1965 and 1956 cm^{-1}, MS : m/z 688 $[M^+]$, 604 $[M^+-3CO]$, 520 $[M^+-6CO]$, 436 $[M^+-9CO]$, 352 $[M^+-12CO]$, 324 $[Fe_3S_4CO]^+$, 256 $[Fe_4S]^+$, 240 $[Fe_4S_4]^+$, 152 $[FeS_3]^+$, 144 $[Fe_2S]^+$, 140 $[Fe(CO)_3]^+$, 120 $[FeS_2]^+$, 88 $[FeS]^+$, 56 $[Fe]^+$.

Reaction of $Na_2[Fe(CO)_4]$ with SCl_2

To a suspension of $Na_2[Fe(CO)_4]$ (1.09 g, 5.1 mmol) in THF (40 mL) was added a solution of SCl_2 (0.525 g, 5.10 mmol) in the same solvent (30 mL) at room temperature with stirring under nitrogen atmosphere. After completion of addition, the reaction mixture was heated to reflux (66°C) for 6 hours. The progress of the reaction was followed by analytical TLC. The solvent was then removed *in vacuo* and the residue extracted with diethyl ether and filtered on kieselguhr. The filtrate was concentrated and chromatographed over a column of silica gel (230-400 mesh). Elution with diethyl ether gave a single red band. The band on removal of solvent yielded $[Fe_4S_4(CO)_{12}]$ (**2**) as dark red crystals (0.57 g, 65%, m.p. 108-110°C). The complex is insoluble in nonpolar hydrocarbon solvents i.e. n-pentane, n-hexane, cyclohexane, petroleum ether (40-60°C) etc. IR (diethyl ether, vCO): 2070, 2049, 2024, 2010, 2002, 1983 and 1966 cm^{-1} ; MS : m/z 688 $[M^+]$, 660 $[M^+-CO]$, 548 $[M^+-5CO]$, 464 $[M^+-8CO]$, 408 $[M^+-10CO]$, 380 $[M^+-11CO]$, 352 $[M^+-12CO]$, 288 $[Fe_4S_2]^+$, 232 $[Fe_3S_2]^+$, 176 $[Fe_2S_2]^+$, 152 $[FeS_3]^+$, 144 $[Fe_2S]^+$, 140 $[Fe(CO)_3]^+$, 128 $[S_4]^+$, 120 $[FeS_2]^+$, 88 $[FeS]^+$, 64 $[S_2]^+$ and 56 $[Fe]^+$.

Reaction of $[Fe_4S_4(CO)_{12}]$ (**1**) with PPh_3

A hexane solution (30 mL) of $[Fe_4S_4(CO)_{12}]$ (0.10 g, 0.145 mmol) and PPh_3 (0.038 g, 0.145 mmol) heated to reflux for 12 hours during which it was changed from red to light brown. Solvent was then removed and the reaction mass was chromatographed over a column of silica gel (230-400 mesh). Elution with pet. ether (40-60°C) gave a reddish-brown band. The band on removal of solvent afforded $[Fe_4S_4(CO)_{11}(PPh_3)]$ (3) as reddish-brown crystals (0.064 g, 48%, m.p. 101-102°C); IR (cyclohexane, vCO): 2071, 2052,

2031, 2004, 1983, 1960, 1946 and 1923 cm^{-1} ; ^{1}H NMR (CDCl$_3$) : δ 7.6-7.39 (m, 15H); MS : m/z 922 [M$^+$ not observed], 660 [M$^+$-P(C$_6$H$_5$)$_3$], 632 [M$^+$-{P(C$_6$H$_5$)$_3$ + CO}], 604 [M$^+$-{P(C$_6$H$_5$)$_3$ + 2CO}], 548 [M$^+$-{P(C$_6$H$_5$)$_3$ + 4CO}], 464 [M$^+$-{P(C$_6$H$_5$)$_3$ + 7CO}], 436 [M$^+$-{P(C$_6$H$_5$)$_3$ + 8CO}], 408 [M$^+$-{P(C$_6$H$_5$)$_3$ + 9CO}], [M$^+$-{P(C$_6$H$_5$)$_3$ + CO}], 380 [M$^+$-{P(C$_6$H$_5$)$_3$ + 10CO}], 352 [M$^+$-{P(C$_6$H$_5$)$_3$ + 11CO}], 296 [Fe$_3$S$_4$]$^+$, 264 [Fe$_3$S$_3$]$^+$, 232 [Fe$_3$S$_2$]$^+$, 200 [Fe$_3$S]$^+$, 88 [FeS]$^+$, 56 [Fe]$^+$, 262 [P(C$_6$H$_5$)$_3$]$^+$, 185 [P(C$_6$H$_5$)$_2$]$^+$, 108 [P(C$_6$H$_5$)]$^+$, 31 [P]$^+$.

Decomposition reaction of [Fe$_4$S$_4$(CO)$_{12}$] (2) into [Fe$_3$(CO)$_{12}$] and elemental Sulfur

The iron-Sulfur cluster [Fe$_4$S$_4$(CO)$_{12}$] is insoluble in most of the common organic solvents like n-pentane, n-hexane, petroleum ether (40-60°C), cyclohexane etc; in which cluster **2** decomposed rapidly (about 5-10 minutes) into [Fe$_3$(CO)$_{12}$] and Sulfur. [Fe$_3$(CO)$_{12}$] remains as green solution while Sulfur precipitates as yellow solid (m.p. 112-114°C). In diethyl ether, the cluster **2** also decomposed but slowly (about 22 hours), in a similar manner to give Fe$_3$(CO)$_{12}$ solution and solid component.

Results and Discusion

The reaction of Na$_2$[Fe(CO)$_4$] with elemental Sulfur in THF at refluxing condition under nitrogen atmosphere for 6 hours resulted in the isolation of [Fe$_4$S$_4$(CO)$_{12}$] (**1**) as rubyred crystals in 45% yield. The IR spectrum of **1** in cyclohexane exhibited νCO bands at 2083, 2062, 2042, 2006, 1990, 1965 and 1956 cm^{-1}. These bands are regarded as terminal νCO stretching frequencies (1800-2140 cm^{-1}) [20]. The significant upward shifts in vibrational frequencies [from 1790 cm^{-1} for Na$_2$[Fe(CO)$_4$][21] clearly indicates the formation of neutral complex. These spectral pattern are also characteristics of the cluster complex with terminal carbonyls. Moreover, the carbonyl absorption of 1 are similar to those observed for Fe-S cluster complex [Fe$_4$(HSCH$_2$CH$_2$SH)$_2$(CO)$_{12}$] [22].

The mass spectrum of **1** showed the molecular ion peak M$^+$ at m/z 688 corresponding to molecular formula [Fe$_4$S$_4$(CO)$_{12}$]. Other important peaks at 604, 520, 436, 352 are due to the sequential loss of three, six, nine and twelve CO groups from molecular ion peak (M$^+$). The mass fragmentation pattern of the complex **1** may be represented schematically as follows (Scheme 1) is in agreement with the proposed formula for [Fe$_4$S$_4$(CO)$_{12}$].

Thus on the basis of the spectral evidences the structure of the compound is proposed as 1, shown in scheme I.

$$Na_2[Fe(CO)_4] \; + \; S_8 \xrightarrow[\text{6hrs, reflux}]{\text{THF}}$$

(1)
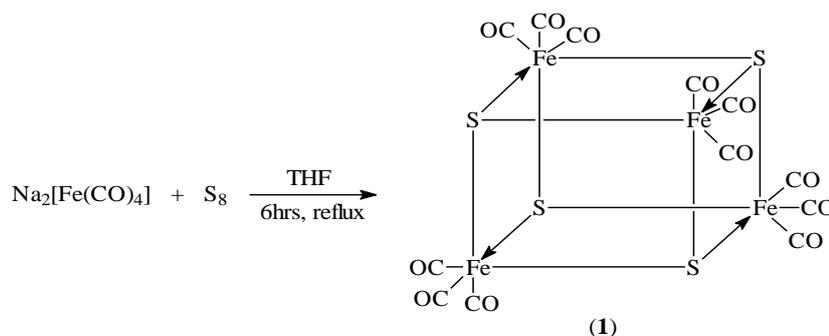
Scheme I

The reaction of $Na_2[Fe(CO)_4]$ with SCl_2 in refluxing THF under nitrogen atmosphere for 6 hours resulted $[Fe_4S_4(CO)_{12}]$ (**2**) as dark red crystalline complex in 65% yield. The IR spectrum of **2** in diethyl ether exhibited νCO bands at 2070, 2049, 2024, 2010, 2002, 1983 and 1966 cm^{-1}. These bands are regarded as terminal carbonyl stretching frequencies.[20] The significant upward shifts in vibrational frequencies [from 1790 cm^{-1} for $Na_2[Fe(CO)_4]$[21] is a clear indication of the formation of a neutral complex. The IR spectral pattern is also characteristics of the cluster complex with terminal carbonyl groups. The νCO frequencies are similar to those reported for cluster complex.[22]

The mass spectrum of **2** showed the molecular ion peak at m/z 688, corresponding to the molecular formula $[Fe_4S_4(CO)_{12}]$. Other important peaks at 660, 548, 464, 408, 380 and 352 are due to the successive loss of one, five, eight, ten, eleven and twelve CO groups from M^+. The mass fragmentation pattern is in agreement with proposed complex **2**.

Thus on the basis of the spectral evidences the structure of the compound is proposed as 2, shown in scheme II.


$$Na_2[Fe(CO)_4] \ + \ SCl_2 \xrightarrow[\text{6hrs, reflux}]{\text{THF}}$$

(**2**)
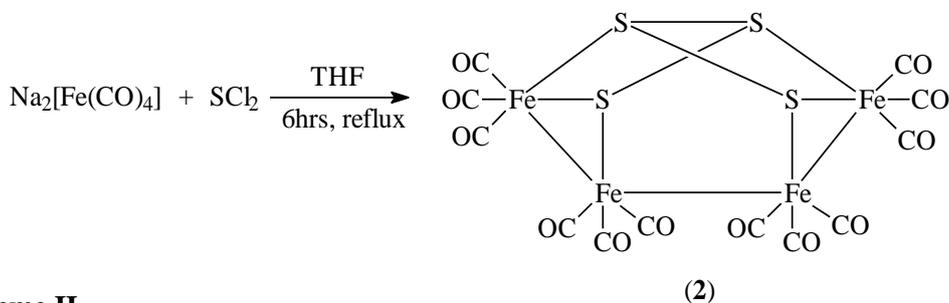
Scheme II

The reaction of $[Fe_4S_4(CO)_{12}]$ (**2**) with PPh_3 (1:1 molar ratio) in refluxing cyclohexane for 12 hours under nitrogen atmosphere gave a reddish-brown solution. Usual work up of the reaction mass and chromatographic separation as detailed in the experimental section resulted in the isolation of reddish-brown crystals of $[Fe_4S_4(CO)_{11}(PPh_3)]$ (**3**) in 48% yield. The complex has been characterized by IR, ^{1}H NMR and mass spectroscopic data.

The IR spectrum of **3** in $CDCl_3$ exhibited bands at 2071, 2052, 2031, 1983, 1960, 1946 and 1923 cm^{-1} in terminal carbonyl stretching region[20]. The drop in νCO frequencies [from 2083, 2062, 2042, 2006, 1990, 1965 cm^{-1} for $[Fe_4S_4(CO)_{12}]$ to 2071, 2052, 2031, 2004, 1983, 1960, 1946 and 1923 cm^{-1} confirm the formation of a new complex. The shifting of νCO frequencies to lower values can be accounted for by the fact that the ligand PPh_3 is a σ-donor and has essentially no ability to back accept and hence increase the M-C bond orders and shifts the remaining CO frequencies to lower values.

The ^{1}H NMR spectrum of **3** in $CDCl_3$ exhibited signals at δ 7.6-7.39 as a multiplet. The multiplet at δ 7.6-7.39 is due to aromatic protons of PPh_3. The multiplet at δ 7.6-7.39 clearly indicates the formation of new complex, in which PPh_3 unit is attached to the Fe atom by direct substitution of one CO group.

Based on the proposed molecular formula the mass spectrum is expected to exhibit molecular ion (M^+) peak at m/z 922. But loss of some part of the complex is energetically most facile and therefore no parent molecular ion (M^+) peak is observed. The highest peak observed at m/z 660 is due to loss of PPh_3 from the parent molecular ion peak [m/z 922]. The mass fragmentation pattern is in agreement with the proposed molecular formula.

Thus on the basis of the spectral evidences the structure of the compound is proposed as 3, shown in scheme III.

$$[Fe_4S_4(CO)_{12}] + PPh_3 \xrightarrow[\text{12 hrs, reflux}]{\text{cyclohexane}}$$

(**1**)

( )
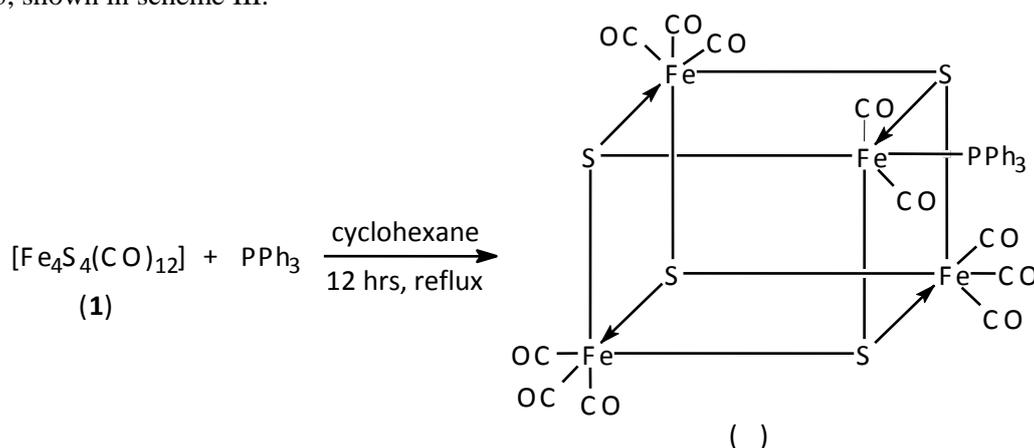
Scheme III

The iron-Sulfur cluster $[Fe_4S_4(CO)_{12}]$ (**2**) is insoluble in most of the common organic solvents like n-pentane, n-hexane, petroleum ether (40-60°C), cyclohexane etc. However, in the above mentioned solvents, cluster **2** decomposed rapidly giving $[Fe_3(CO)_{12}]$ as green solution and elemental Sulfur as yellow precipitate. Cluster **2** also decomposed in diethyl ether, but slowly, in a similar manner to give $[Fe_3(CO)_{12}]$ solution and elemental Sulfur. $[Fe_3(CO)_{12}]$ has been characterized by IR and elemental Sulfur has been identified by lead acetate and sodium nitropruside test.

Characterization of $Fe_3(CO)_{12}$

The IR spectrum of the green solution exhibited νCO bands at 2047, 2025, 1997, 1867 and 1835 cm^{-1}, which are similar to those of an authentic sample of $[Fe_3(CO)_{12}]$ (νCO, 2046, 2023, 1867 and 1835 cm^{-1}).[26]
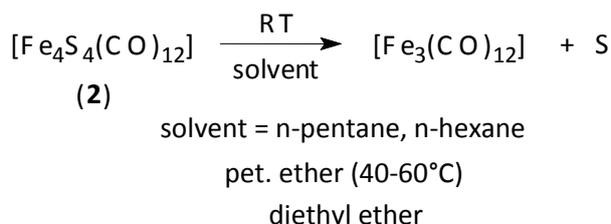
Identification of the solid component

Elemental Sulfur has been identified using the sodium fusion solution of yellow residue with lead acetate and sodium nitropruside solution saperately by the following methods.

1. 1 mL of the fusion solution was acidified with dilute acetic acid and was added a few drops of lead acetate solution. A black precipitate of lead sulphide indicated the presence of Sulfur.

2. To 1 mL of the fusion solution was added 2-3 drops of a freshly prepared dilute solution (0.1%) disodiumpentacyanonitrosylferrate, $Na_2[Fe(CN)_5NO]$. Formation of a purple colouration which fades on standing indicated the presence of Sulfur.

Thus on the basis of IR and the above chemical tests with lead acetate and sodium nitropruside, it is evident that $[Fe_3(CO)_{12}]$ and Sulfur were formed by the decomposition of cluster $[Fe_4S_4(CO)_{12}]$ (**2**) as shown in scheme IV.

$$[Fe_4S_4(CO)_{12}] \xrightarrow[\text{solvent}]{RT} [Fe_3(CO)_{12}] + S$$

(**2**)

solvent = n-pentane, n-hexane

pet. ether (40-60°C)

diethyl ether

Scheme IV

Conclusion

We have described the systhesis of Fe-S cluster complexes 1 and 2 having different structures from the reactions of $Na_2[Fe(CO)_4]$ with elemental Sulfur and SCl_2 respectively. Complex 1 having ferredoxin analogue structure is found to be stable, while complex 2 having butterfly structure is found to be unstable. Complex 3, the derivative of complex 1 is also found to be stable. Electron counts shows that all of them satisfy the 18 eletron rule. Work in this respect is in progress and will be reported elsewhere.

Acknowledgement

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