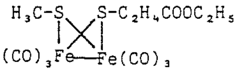
09.5-1 CRYSTAL AND MOLECULAR STRUCTURES OF A SERIES OF Fe-S CLUSTER COMPLEXES $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$.

By Yao Xinkan, Wang Ruji and Wang Honggen, Analysis And Computer Center, Nankai University, Tianjin, P.R. China, and Song Licheng, Hu Qingmei and Wang Jitao, Department of Chemistry, Nankai University, Tianjin, P.R. China.

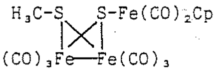
The influences of the different substituents R^1 and R^2 on the structures of eight Fe-S cluster complexes $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$ were studied. Their chemical structure diagrams and crystal data are as follows:

(I)



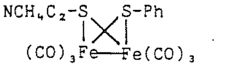
a=7.944, b=8.165
c=14.890Å, α=82.37,
β=77.99, γ=71.25°,
triclinic, $P\bar{1}$,
Z=2, R=0.023.

(II)



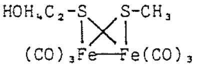
a=7.9099, b=10.774
c=22.531Å, γ=92.91°,
(unique axis C)
monoclinic, $P2_1/n$,
Z=4, R=0.024.

(III)



a=11.175, b=11.877,
c=15.640Å, α=106.19,
β=103.15, γ=98.46°,
triclinic, $P\bar{1}$,
Z=4, R=0.028.

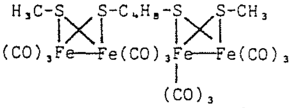
(IV)



a=15.784, b=22.172,
c=9.774Å, β=119.53°,

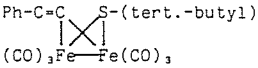
monoclinic, C2/c ,
Z=8, R=0.077.

(V)



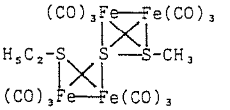
a=7.910, b=12.564,
c=14.644Å, β=101.28°,
monoclinic, $P2_1/a$
Z=2, R=0.035.

(VI)



a=15.145, b=9.151,
c=16.198Å, β=113.45°,
monoclinic, $P2_1/n$,
Z=4, R=0.074.

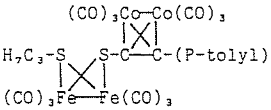
(VII)



a=11.875, b=12.920,
c=17.020Å,

orthorhombic, $P2_12_12_1$,
Z=4, R=0.036.

(VIII)



a=9.139, b=9.610,
c=17.183Å, α=84.36
β=89.45, γ=88.15°,
triclinic, $P\bar{1}$,
Z=2, R=0.072

The Fe-Fe distances are almost constant (2.505,2.518Å) except the structures VI and VII in which the Fe-Fe distances are 2.526 (VI) and 2.542Å (VII). Mössbauer spectroscopy of VI has established that two Fe atoms of VI have the same coordinate environment, so probably one of two Fe atoms of VI is bonded to the π-bond of the ethylene. Fe atoms keep the six-coordinate distorted octahedral geometry in each complex.

There is a trend (Song Licheng et al., Acta Chimica Sinica, 1986, 44, 558) that the more the difference between R^1 and R^2, the more obvious the unequivalency of the Fe-S distances, but it is not large.

The carbonyls appear in the overlapping conformation owing to the steric obstruction effect of S atoms, but it has been disturbed partially in VI because of the presence of the ethylene.

The conformation of R^1 and R^2 are (a,e) type for the majority of these complexes.

09.5-2 CONFIGURATION AND STRUCTURAL PARAMETERS OF SULPHUR-CONTAINING IRON CARBONYL CLUSTERS FORMED VIA VARIOUS THIONES.

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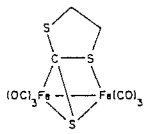
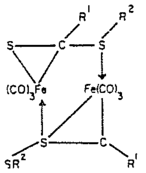
Pentacarbonyl iron or nonacarbonyl diiron react photochemically with thioketone derivatives of the type S=C(X)Y to produce di- and multinuclear iron carbonyl clusters. The reaction of the trithiocarbonate $S{=}CS(CH_2)_2S$ with $[Fe(CO)_5]$ gives the metal-metal bonded complex $[Fe_2(CO)_6\{\mu\text{-}\eta^2\text{-}SCS(CH_2)_2S\text{-}S,S'\}]$ (Fe-Fe)(I) with doubly bridged iron atoms. The reaction of S=C(Ph)SMe with $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ gives $[Fe(CO)_3\{SC(Ph)SMe\}]_2$(II), an asymmetric dimer containing no metal-metal bond, and $[Fe_2(CO)_6\{SC(Ph)C(O)SMe\}]$ (III), a metal-metal bonded complex in which carbonyl insertion into the C-SMe bond occured. The reaction with $S{=}C(NEt_2)SEt$ gives $[\{Fe_2(CO)_6\}_3(\mu_4\text{-}S)(\mu\text{-}CNEt_2)_2]$ 3(Fe-Fe) (IV), a complex containing three metal-metal bonded $Fe_2(CO)_6$ units linked by bridging sulphur atoms in butterfly configuration. The crystal structures will be presented and the geometries and structural parameters discussed.

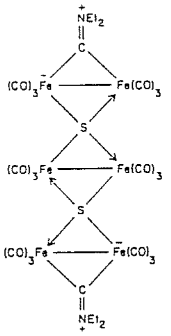


I

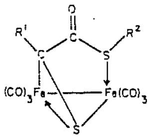


R¹ = Ph , R² = Me

II



IV



R¹ = Ph , R² = Me

III