



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 682 (2003) 59–65

Journal  
of Organo  
metallic  
Chemistry

www.elsevier.com/locate/jorganchem

# Mixed metal pentanuclear clusters $[MFe_4S_4(CO)_{12}]^{z-}$ ( $M = V, Mn$ and $Cr; z = 0, 2$ ) and X-ray crystal structures of $[VFe_4S_4(CO)_{12}]$ and $[MnFe_4S_4(CO)_{12}]^{2-}$

Botao Zhuang\*, Jun Chen, Lingjie He, Haofeng Sun, Zhangfeng Zhou,  
Chensheng Lin, Kechen Wu, Zixiang Huang

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou,  
Fujian 350002, China

Received 26 May 2003; received in revised form 14 July 2003; accepted 14 July 2003

## Abstract

Reaction of  $VCl_3$ ,  $MnCl_2$  and  $CrCl_3 + Zn$  with  $[Fe_2S_2(CO)_6]^{2-}$ , from reduction of  $[Fe_2S_2(CO)_6]$  by  $LiEt_3BH$ , resulting in pentanuclear mixed metal clusters  $[VFe_4S_4(CO)_{12}]$  (**1**),  $[Et_4N]_2[MnFe_4S_4(CO)_{12}]$  (**2**) and  $[Et_4N]_2[CrFe_4S_4(CO)_{12}]$  (**3**), respectively. Complexes **1**, **2** and **3** have been characterized by elemental analysis, spectroscopy and the crystal structures of **1** and **2** have been determined by X-ray crystallography. The structures of **1** and **2** contain a penta-nuclear  $M-Fe-S$  core,  $[Fe_2S_2MS_2Fe_2]^{z-}$  ( $M = V, z = 0$  (**1**) and  $M = Mn, z = 2$  (**2**)), consisting of two  $[Fe_2S_2]$ -units chelating to a metal atom. The two  $[Fe_2S_2]$  units are in 'butterfly' type configuration like the one in  $[Fe_2S_2(CO)_6]^{2-}$ . In **1** there are four  $V-Fe$  bonds of 2.822–2.865 Å, but in **2** there were no  $Mn-Fe$  bonds found.  $V-S$  distances are 2.205–2.210 Å and  $Mn-S$  bond lengths are 2.358–2.380 Å. The novel structural configuration, IR spectra and synthesis were discussed.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:**  $M(V, Mn, Cr)-Fe-S$  cluster compounds; Synthesis and structures; IR spectra

## 1. Introduction

Diirondisulfurhexacarbonyl,  $[Fe_2S_2(CO)_6]$ , especially its dianion  $[Fe_2S_2(CO)_6]^{2-}$  [1–5], is very useful and significant for obtaining mixed-valence and mixed-metal polynuclear metal cluster complexes, and the chemistry of  $[Fe_2S_2(CO)_6]$  and the reaction involving its anion,  $[Fe_2S_2(CO)_6]^{2-}$ , have been followed extensively with interest. A variety of metal cluster complexes with different type of  $[Fe_2S_2]$ -units have been synthesized by reaction of  $[Fe_2S_2(CO)_6]$  or  $[Fe_2S_2(CO)_6]^{2-}$  with metal carbonyl species and characterized by X-ray crystallography. Two types of  $[Fe_2S_2]$ -units have been observed in the cluster compounds obtained, They are 'butterfly' type  $[Fe_2S_2]$  (A) for example in  $[MoOFe_5S_6(CO)_{12}]^{2-}$  [6] and  $[Cu_5Fe_6S_6(CO)_{18}(PPh_3)_2]^-$  [7] and plane type one

(B), for instance, in  $[Fe_2Mo(CO)_8Se_2Te_2]$  [8] and  $[MFe_2S_2(CO)_8(S_2CNEt_2)]^-$  ( $M = Mo$  and  $W$ ) [9]. We recently paid attention to the reaction of  $[Fe_2S_2(CO)_6]^{2-}$  with some what higher valence metal halides in order to approach the reason for formation of this two types of  $[Fe_2S_2]$ -units in cluster complexes and to obtain new conformation of  $M-Fe-S$  cluster compounds. Herein are reported the mixed-metal penta-nuclear  $M-Fe-S$  clusters,  $[MFe_4S_4(CO)_{12}]^{z-}$  ( $M = V, z = 0$  (**1**);  $M = Mn, z = 2$  (**2**); and  $M = Cr, z = 2$  (**3**)) synthesized from the reaction of  $[Fe_2S_2(CO)_6]^{2-}$  with  $VCl_3$ ,  $MnCl_2$  and  $CrCl_3 + Zn$ , respectively.

## 2. Results and discussion

### 2.1. The crystal structure of $[VFe_4S_4(CO)_{12}]$ (**1**)

The selected bond distances and bond angles of **1** are listed in Table 1. The molecular structure of **1** is depicted

\* Corresponding author. Tel.: +86-591-3792-464; fax: +86-591-3714-946.

E-mail address: zbt@ms.fjirsm.ac.cn (B. Zhuang).

Table 1  
Selected bond lengths (Å) and bond angles (°) for  $[\text{VFe}_4\text{S}_4(\text{CO})_{12}]$  (**1**)

Bond lengths			
Fe(1)–C(1)	1.797(5)	Fe(3)–C(7)	1.825(5)
Fe(1)–C(3)	1.806(5)	Fe(3)–S(3)	2.2908(11)
Fe(1)–C(2)	1.812(4)	Fe(3)–S(4)	2.2996(11)
Fe(1)–S(2)	2.2987(11)	Fe(3)–Fe(4)	2.5208(7)
Fe(1)–S(1)	2.3010(11)	Fe(3)–V	2.8550(8)
Fe(1)–Fe(2)	2.5060(7)	Fe(4)–C(11)	1.794(5)
Fe(1)–V	2.8251(8)	Fe(4)–C(10)	1.803(5)
Fe(2)–C(4)	1.791(5)	Fe(4)–C(12)	1.809(4)
Fe(2)–C(5)	1.791(5)	Fe(4)–S(3)	2.2958(11)
Fe(2)–C(6)	1.822(5)	Fe(4)–S(4)	2.3049(11)
Fe(2)–S(2)	2.2922(11)	Fe(4)–V	2.8220(8)
Fe(2)–S(1)	2.3059(11)	V–S(1)	2.2052(11)
Fe(2)–V	2.8648(8)	V–S(4)	2.2059(12)
Fe(3)–C(9)	1.797(5)	V–S(3)	2.2094(11)
Fe(3)–C(8)	1.799(5)	V–S(2)	2.2098(12)
Bond angles			
S(2)–Fe(1)–Fe(2)	56.79(3)	S(3)–V–Fe(4)	52.60(3)
S(1)–Fe(1)–Fe(2)	57.14(3)	S(2)–V–Fe(4)	105.85(3)
S(2)–Fe(1)–S(1)	89.31(4)	S(1)–V–Fe(1)	52.71(3)
S(2)–Fe(1)–V	49.81(3)	S(4)–V–Fe(1)	161.04(4)
S(1)–Fe(1)–V	49.68(3)	S(3)–V–Fe(1)	104.84(4)
Fe(2)–Fe(1)–V	64.69(2)	S(2)–V–Fe(1)	52.62(3)
S(2)–Fe(2)–S(1)	89.35(4)	Fe(4)–V–Fe(1)	140.80(3)
S(2)–Fe(2)–Fe(1)	57.04(3)	S(1)–V–Fe(3)	107.30(3)
S(1)–Fe(2)–Fe(1)	56.95(3)	S(4)–V–Fe(3)	52.15(3)
S(2)–Fe(2)–V	49.22(3)	S(3)–V–Fe(3)	51.90(3)
S(1)–Fe(2)–V	49.04(3)	S(2)–V–Fe(3)	158.56(4)
Fe(1)–Fe(2)–V	63.06(2)	Fe(4)–V–Fe(3)	52.720(18)
S(3)–Fe(3)–S(4)	89.50(4)	Fe(1)–V–Fe(3)	143.38(3)
S(3)–Fe(3)–Fe(4)	56.76(3)	S(1)–V–Fe(2)	52.15(3)
S(4)–Fe(3)–Fe(4)	56.91(3)	S(4)–V–Fe(2)	108.83(4)
S(3)–Fe(3)–V	49.37(3)	S(3)–V–Fe(2)	157.05(4)
S(4)–Fe(3)–V	49.24(3)	S(2)–V–Fe(2)	51.76(3)
Fe(4)–Fe(3)–V	62.97(2)	Fe(4)–V–Fe(2)	145.04(3)
S(3)–Fe(4)–S(4)	89.24(4)	Fe(1)–V–Fe(2)	52.257(18)
S(3)–Fe(4)–Fe(3)	56.56(3)	Fe(3)–V–Fe(2)	144.89(3)
S(4)–Fe(4)–Fe(3)	56.70(3)	V–S(1)–Fe(1)	77.62(4)
S(3)–Fe(4)–V	49.86(3)	V–S(1)–Fe(2)	78.81(4)
S(4)–Fe(4)–V	49.72(3)	Fe(1)–S(1)–Fe(2)	65.91(3)
Fe(3)–Fe(4)–V	64.31(2)	V–S(2)–Fe(2)	79.02(4)
S(1)–V–S(4)	119.56(5)	V–S(2)–Fe(1)	77.58(4)
S(1)–V–S(3)	115.53(4)	Fe(2)–S(2)–Fe(1)	66.17(3)
S(4)–V–S(3)	94.09(4)	V–S(3)–Fe(3)	78.73(4)
S(1)–V–S(2)	94.15(4)	V–S(3)–Fe(4)	77.54(4)
S(4)–V–S(2)	116.95(5)	Fe(3)–S(3)–Fe(4)	66.68(3)
S(3)–V–S(2)	118.58(5)	V–S(4)–Fe(3)	78.61(4)
S(1)–V–Fe(4)	159.88(4)	V–S(4)–Fe(4)	77.42(4)
S(4)–V–Fe(4)	52.86(3)	Fe(3)–S(4)–Fe(4)	66.39(3)

in Fig. 1. As is shown in Table 1 and Fig. 1, **1** contains a penta-nuclear mixed-metal cluster core  $[\text{VFe}_4\text{S}_4]$  (A), in which two  $[\text{Fe}_2\text{S}_2]^{2-}$ -units chelate to a V atom by four S atoms resulting in distorted tetrahedral coordination of V atom with S–V–S ‘bite’ angles of  $94.12^\circ$  and remaining S–V–S angles of  $117.54^\circ$  (average). Around the core there are 12 carbonyls (every three carbonyls coordinate to each Fe atom). The Fe–S bond lengths of  $2.29228(12)$ – $2.3052(11)$  Å, Fe–Fe bond distances of  $2.5059(7)$ – $2.5208(8)$  Å and Fe–S–Fe angle of  $65.92(3)$ –

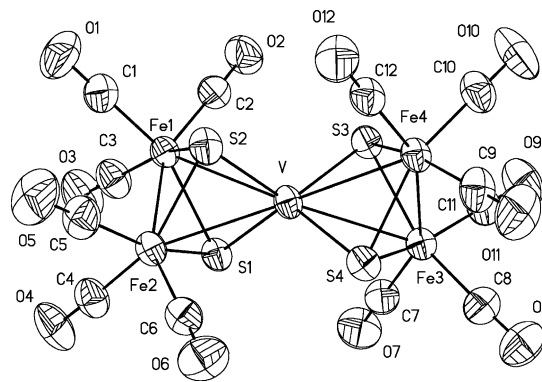


Fig. 1. The structure of  $[\text{VFe}_4\text{S}_4(\text{CO})_{12}]$  (**1**)

$66.69(3)^\circ$  in the  $[\text{Fe}_2\text{S}_2]$ -units of complex **1** are comparable with those in  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  ( $2.222$ – $2.238$  Å,  $2.552$  Å and  $69.67$ – $70.08^\circ$ ) [1] implying that the valence of Fe atoms are the same as in  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  ( $\text{Fe}^I$ ) and the valence of V is +4. The Fe–V distances of  $2.8221(8)$ – $2.8648(8)$  Å indicate the metal–metal interaction between Fe and V atoms. Thus, the structure of the whole core can be considered as a polyhedron consisted of two face-sharing bi-tetrahedrons with a sharing apex (V atom). This is a new conformation which is very different from the reported  $\text{Fe}_2\text{S}_2(\text{CO})_6$ -containing complexes Mo-compound,  $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$  [8], Ni-compound,  $[\text{NiFe}_4(\text{CO})_{12}\text{S}_4]$  [10] and Fe-compound,  $[\text{Fe}_5\text{S}_4(\text{CO})_{12}]^{2-}$  [11]. The Mo-compound,  $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$ , has a core consisted of two square pyramids with a common apex (Mo atom) [8]. In another word, the  $[\text{Fe}_2\text{S}_2]$ -units in **1** are butterfly type with Fe–Fe bond length of  $2.51$  Å and in  $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$  are planar type without any Fe–Fe interaction. The valence of Fe in **1** are +1 and the one in  $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$  are +2. For the Ni-compound,  $[\text{NiFe}_4(\text{CO})_{12}\text{S}_4]$  [10] and Fe-compound,  $[\text{Fe}_5\text{S}_4(\text{CO})_{12}]^{2-}$  [11], although they possess butterfly type  $\text{Fe}_2\text{S}_2(\text{CO})_6$ -units, there is no interaction between the central atoms (Ni, Fe) and Fe atoms of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  ligands. Forming a sharp contrast, compound **1** has four very strong V–Fe bonds. Its is worth pointing out that the V–S bond distances of  $2.208$  Å (average) in **1** is shorter than that in other reported V– $\text{Fe}_2\text{S}_2(\text{CO})_6$  complexes for example  $(\text{MeCpV})_2[\text{Fe}_2\text{S}_2(\text{CO})_6]$  (av.  $2.48$  Å) [12] and  $[\text{CpVO-Fe}_2\text{S}_2(\text{CO})_6]$  (av.  $2.268$  Å) [13] and that in cubane-like V–Fe–S cluster  $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{MeCN})_3]^-$  (av.  $2.33$  Å) [14]. This may be due to both the higher oxidation state of V atom and V–Fe interaction in **1**. The skeleton electron number of compound **1** is 77. Using density function theory (ADF) [15] to calculate molecule of compound **1**, the ADF result shows that the orbital energies of HOMO and LUMO are  $-5.399$  eV and  $-4.427$  eV, respectively, and the HOMO is occupied by the unpaired electron and its main component is contributed

from d orbital of V atom. In our knowledge, **1** has the highest Fe/V ratio among the V–Fe–S complexes reported so far. This might be useful for investigating and simulating the active center in the V–Fe–S protein.

## 2.2. The crystal structure of $[E_4N]_2[MnFe_4S_4(CO)_{12}]$ (**2**)

Crystal structure determination of compound **2** showed that there are four sets of molecules in a cell and each set consists of three similar molecules  $[Et_4N]_2[MnFe_4S_4(CO)_{12}]$  in some what different bond distances and angles. The selected bond lengths and bond angles are shown in Table 2 and the molecular structure of the anion of **2** is depicted in Fig. 2. As shown in Table 2 and Fig. 2, the structure of the anion of **2** contains a penta-nuclear  $[MnFe_4S_4]^{2-}$  core (B), which is different from that of compound **1**, with nonbonding of Fe and Mn atoms (3.147–3.330 Å). The geometry around the Mn atom is distorted tetrahedral with S–Mn1–S ‘bite’ angle of 81.07° (average) and remaining S–Mn1–S angle of 124.53° (average). Thus, the structure of compound **2** is more similar to the

one of  $[Fe_5S_4(CO)_{12}]^{2-}$  [11]. However, this is a new conformation of Mn-complexes containing  $Fe_2S_2(CO)_6$  ligands which is very different from the reported Mn– $[Fe_2S_2(CO)_6]$  compound,  $Mn_2(CO)_8S_2Fe_2(CO)_6$  [16]. The  $[Fe_2S_2]$ -units with Fe–S of  $\sim 2.30$  Å, Fe–Fe of 2.48–2.50 Å, and Fe–S–Fe of 65.14–65.99° are comparable with that in compound **1** implying that the valence of the Fe atoms in compound **2** are the same as that in compound **1** and  $[Fe_2S_2(CO)_6]$ . Thus, the Fe atoms in **2** should be in +1 and the Mn atom of **2** is +2. Owing to the longer Mn–S bond distances (2.38–2.39 Å) and nonbonding of Mn and Fe atoms, the tetrahedral coordination of Mn atom in complex **2** became more distorted than that of V atom in complex **1** and the central Fe atom in  $[Fe_5S_4(CO)_{12}]^{2-}$  [11].

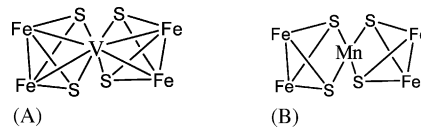


Table 2  
Selected bond lengths (Å) and bond angles (°) for  $[Et_4N]_2[MnFe_4S_4(CO)_{12}]$  (**2**)

Bond lengths			
Mn(1)–S(14)	2.358(2)	Fe(12)–S(11)	2.294(2)
Mn(1)–S(11)	2.377(2)	Fe(12)–S(12)	2.309(2)
Mn(1)–S(13)	2.379(2)	Fe(13)–C(133)	1.743(8)
Mn(1)–S(12)	2.380(2)	Fe(13)–C(132)	1.758(9)
Fe(11)–C(111)	1.759(8)	Fe(13)–C(131)	1.787(9)
Fe(11)–C(113)	1.766(7)	Fe(13)–S(14)	2.292(2)
Fe(11)–C(112)	1.773(7)	Fe(13)–S(13)	2.313(2)
Fe(11)–S(11)	2.2994(19)	Fe(13)–Fe(14)	2.4820(17)
Fe(11)–S(12)	2.300(2)	Fe(14)–C(141)	1.694(10)
Fe(11)–Fe(12)	2.5013(13)	Fe(14)–C(142)	1.740(9)
Fe(12)–C(123)	1.745(9)	Fe(14)–C(143)	1.754(9)
Fe(12)–C(121)	1.745(8)	Fe(14)–S(13)	2.289(2)
Fe(12)–C(122)	1.773(9)	Fe(14)–S(14)	2.299(2)
Bond angles			
S(14)–Mn(1)–S(11)	127.23(8)	S(13)–Mn(1)–S(12)	125.08(8)
S(14)–Mn(1)–S(13)	81.33(7)	S(11)–Mn(1)–S(13)	123.77(8)
S(11)–Mn(1)–S(12)	80.80(7)	S(14)–Mn(1)–S(12)	125.05(8)
S(11)–Fe(11)–S(12)	84.18(7)	S(13)–Fe(14)–Fe(13)	57.83(6)
S(11)–Fe(11)–Fe(12)	56.90(6)	S(14)–Fe(14)–Fe(13)	57.13(7)
S(12)–Fe(11)–Fe(12)	57.30(6)	Fe(12)–S(11)–Fe(11)	65.99(6)
S(11)–Fe(12)–S(12)	84.11(7)	Fe(12)–S(11)–Mn(1)	89.08(8)
S(11)–Fe(12)–Fe(11)	57.11(5)	Fe(11)–S(11)–Mn(1)	85.38(7)
S(12)–Fe(12)–Fe(11)	56.97(6)	Fe(11)–S(12)–Fe(12)	65.73(6)
S(14)–Fe(13)–S(13)	84.18(8)	Fe(11)–S(12)–Mn(1)	85.30(7)
S(14)–Fe(13)–Fe(14)	57.42(7)	Fe(12)–S(12)–Mn(1)	88.66(7)
S(13)–Fe(13)–Fe(14)	56.91(6)	Fe(14)–S(13)–Fe(13)	65.27(6)
S(13)–Fe(14)–S(14)	84.55(7)	Fe(14)–S(13)–Mn(1)	87.44(7)
Fe(13)–S(13)–Mn(1)	85.88(7)	Fe(13)–S(14)–Mn(1)	86.85(7)
Fe(13)–S(14)–Fe(14)	65.45(6)	Fe(14)–S(14)–Mn(1)	87.72(7)

## 2.3. IR spectra of $[VFe_4S_4(CO)_{12}]$ (**1**), $[E_4N]_2[MnFe_4S_4(CO)_{12}]$ (**2**) and $[Et_4N]_2[CrFe_4S_4(CO)_{12}]$ (**3**)

The selected IR data of complexes **1**, **2** and **3** are shown in Table 3. It can be found that the IR spectra, which reflect the  $[Fe_2S_2(CO)_6]$ -units [17], of complexes **1**, **2** and **3** are very similar. This indicates that they should have similar structure. However, it is obvious that the  $\nu_{Fe-C-O}$  of complex **1** somewhat higher than that of compound **2** and **3** if the data are inspected carefully. This implies that the electron density on the Fe atoms in compound **1** is lower than that in compound **2** and **3** resulting in less back-donation of electrons to the  $\pi^*$  of carbonyls. Referring to the structures of **1** and **2** the reason is easy to be understood, there are metal–metal bond between V and Fe in **1** and nonbonding between Mn and Fe atom in **2** so that the electron transfer between Fe atom and V atom in **1** is larger than that between Fe and Mn in **2**. On the other hand, the high oxidation state of  $V^{4+}$  is more favorable to the electron transfer of  $Fe^I \rightarrow V^{IV}$ . This is consistent with the fact that C–O bond lengths of **1** (average 1.13 Å) are somewhat shorter than that of **2** (average 1.15 Å).

Noteworthy, the IR spectra of **2** and **3** are almost the same. This seems to imply that the structure of compound **3** is more like that of compound **2**. However, compound **3** is incompletely characterized, the real structure of **3** needs to be confirmed by crystallography. The effort to obtain the single crystal of compound **3** suitable for crystallography is in progress.

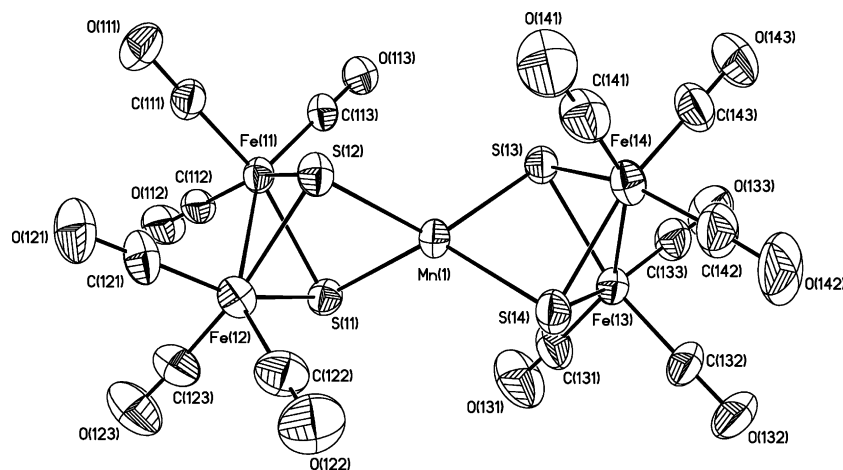


Fig. 2. The molecular structure of the anion  $[\text{Et}_4\text{N}]_2[\text{MnFe}_4\text{S}_4(\text{CO})_{12}]$  (**2**)

Table 3  
The selected IR data of complexes **1**, **2** and **3**

Complexes	$\nu_{\text{FeC-O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{M-S}}$ ( $\text{cm}^{-1}$ )	$\delta_{\text{Fe-C-O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{Fe-CO}}$
<b>1</b>	2081, 2038	–	604, 569	494, 484
	2021, 1996		555	453, 436
<b>2</b>	2044, 2008	336	611, 582	509, 500
	1981, 1963		563	475, 449
<b>3</b>	2044, 2007	336	611, 581	507, 468
	1980, 1963		562	447

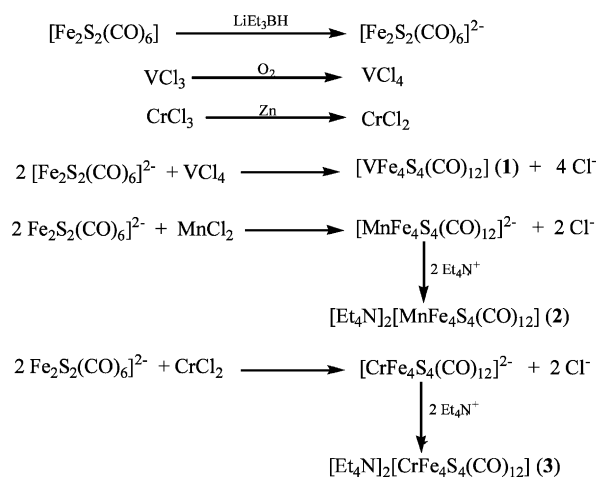
#### 2.4. Synthesis and possible formation pathways of complexes **1**, **2** and **3**

In the light of the results from the studies on the structure and IR spectra, it can be found evidently that: (i) the  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$ -units in compound **1**, **2** and **3** are almost the same as that in the starting material  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  with Fe atom in oxidation state of 1+ and  $[\text{Fe}_2\text{S}_2]$ -unit in butterfly type conformation, indicating that as a reactant  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  did not undergo any redox in the synthetic reaction; (ii) the metal atoms V, Mn and Cr of the complexes are in oxidation state 4+, 2+ and 2+, respectively, indicating that the starting reactants  $\text{VCl}_3$  and  $\text{CrCl}_3$ , respectively, underwent oxidation and reduction in the synthetic reaction systems; (iii) apparently, the reduction of  $\text{CrCl}_3$  to  $\text{CrCl}_2$  is due to the addition of Zn powder because the solution of  $\text{CrCl}_3$  in THF is violet and the  $\text{CrCl}_2$  in THF is light green [18], in fact the color change from violet to green was observed in the synthetic reaction system of compound **3** (see Section 3); (iv) the oxidation of  $\text{VCl}_3$  to  $\text{VCl}_4$  should be an accident which leads to entrance of small amount of air because there is no any oxidant in the synthetic reaction system and the reaction are carried out using a Schlenk technique. This is the reason why the yield was so low for complex **1**. It will be possible to increase the yield of **1** if a proper air entrance

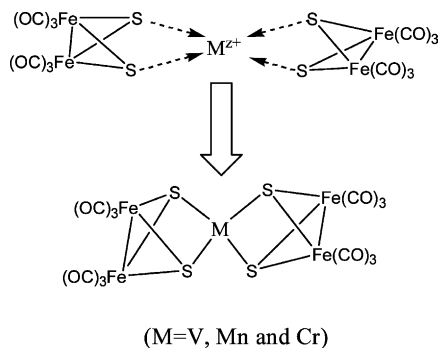
can be controlled. Therefore, the synthetic reactions for complexes **1**, **2** and **3** can be easily figured out as follows in Scheme 1.

As is shown in Scheme 1,  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  undergoes reduction resulting in its di-anion species,  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$ , in the presence of  $\text{LiEt}_3\text{BH}$  [3].  $\text{CrCl}_3$  reacts with Zn giving  $\text{CrCl}_2$ . The  $\text{VCl}_3$  is oxidized by oxygen from the entering air during the accident to give  $\text{VCl}_4$ . In the synthetic reaction of compound **1**, the  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  reacts with  $\text{VCl}_4$  to form  $[\text{VFe}_4\text{S}_4(\text{CO})_{12}]$  (**1**). In the synthetic reaction of compound **2**, the  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  reacts with  $\text{MnCl}_2$  affording  $[\text{MnFe}_4\text{S}_4(\text{CO})_{12}]^{2-}$  which is crystallized as tetraethyl ammonium salt,  $[\text{Et}_4\text{N}]_2[\text{MnFe}_4\text{S}_4(\text{CO})_{12}]$  (**2**). In the synthetic reaction of compound **3**, the  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  reacts with  $\text{CrCl}_2$  resulting in  $[\text{CrFe}_4\text{S}_4(\text{CO})_{12}]^{2-}$  which is collected as tetraethyl ammonium salt  $[\text{Et}_4\text{N}]_2[\text{CrFe}_4\text{S}_4(\text{CO})_{12}]$  (**3**).

Obviously, in the synthetic reactions of compound **1**, **2** and **3**, the whole  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  with butterfly type  $[\text{Fe}_2\text{S}_2]$ -unit is as a reactive fragment to react with metal chloride. Two  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$ , as a bi-dentate ligand,



Scheme 1.



Scheme 2.

chelate to the metal ion ( $V^{4+}$ ,  $Mn^{2+}$  and  $Cr^{2+}$ ) by their four sulfur atoms resulting in four coordination of metal atom in the final products (Scheme 2).

From this results addition to the previous reports about the reaction of  $[Fe_2S_2(CO)_6]^{2-}$  with metal halides, for example,  $NiCl_2$ ,  $PdCl_2$ ,  $PtCl_2$  [19,3],  $CuCl$  [7], and  $MoOCl_5$  [6] resulting in butterfly type  $[Fe_2S_2]$ -unit-containing complexes and with low valent metal carbonyl, for instance,  $Mo(CO)_4I_3$  [20–22] and  $[Mo(CO)_4(S_2CNET_2)]^-$  [9] affording planar type  $[Fe_2S_2]$ -unit-containing complexes, a conclusion seems to be able to reach that the high valence metal ion tends to reacting with intact  $[Fe_2S_2(CO)_6]^{2-}$  containing the butterfly type  $[Fe_2S_2]^{2-}$ -unit and low valence metal atom prefer to reaction with the product containing planar  $[Fe_2S_2]^0$ -unit, which is generated from the disproportionation of  $[[Fe_2S_2(CO)_6]^{2-}$  [9,23].

### 3. Experimental

#### 3.1. Materials and methods

$VCl_3$  and  $MnCl_2$  were purchased from Aldrich,  $CrCl_3$  and  $LiEt_3BH$  were products of Herck–Schuchardt and Fluka, respectively.  $Fe_2S_2(CO)_6$  was prepared by reaction of  $Fe(CO)_5$  with  $Na_2S_5$  and  $KOH$  according to literature method [3]. THF and MeCN were dried by distillation with  $LiAlH_4$  and  $CaH_2$ , respectively. IR spectra were recorded on Nicolet Magna 750 FT-IR infrared spectrophotometer. All reactions and treatment were carried out under nitrogen atmosphere by using Schlenk technique. Elemental analyzer MoD 1106.

#### 3.2. Synthesis of $[VFe_4S_4(CO)_{12}]$ (2)

A 1 M  $LiEt_3Bh$  in THF (1:1 ml) solution was added slowly to a solution of  $Fe_2S_2(CO)_6$  (0.18 g, 0.52 mmol) in 20 ml THF at  $-78^\circ C$  under stirring resulting in a solution color change from red to green. A solution of  $VCl_3$  (0.1 g, 0.63 mmol) in THF (20 ml) was added to this green solution. Removing the cold bath the reaction

temperature slowly rose to room temperature (r.t.) and the reaction mixture was stirred for another 24 h at r.t. resulting in a dark brown solution. After filtering off a small amount of precipitate the filtrate was evaporated in vacuum to dryness. The residue was dissolved in 15 ml of  $CH_2Cl_2$ . After filtering off the insoluble residue, 7 ml of hexane was added to the filtrate. The reaction solution was cooled at  $-10^\circ C$  for 2 weeks. A total of 0.05 g of red–brown plate crystal product  $[VFe_4S_4(CO)_{12}]$  (1) was obtained by filtration, washed with hexane and dried under vacuum. Yield: 26.0% (based on  $[Fe_2S_2(CO)_6]$  used). Elemental Anal. Calc. for  $C_{12}Fe_4VS_4O_{12}$ : V, 6.9; Fe, 30.3, C, 19.5. Found: V, 6.0; 30.5; C, 19.9%. IR (KBr Plate): 2081s, 2038s, 2021s, 1996s  $cm^{-1}$  ( $\nu_{CO}$ ).

#### 3.3. Synthesis of $[Et_4N]_2[MnFe_4S_4(CO)_{12}]$ (2)

$LiEt_3BH$  (1 M) in THF (1.5 ml) was slowly added to a solution of  $Fe_2S_2(CO)_6$  (0.69 g, 2.0 mmol) in THF (20 ml) at  $-78^\circ C$  resulting in a color change of the mixture solution from red to green. Anhydrous  $MnCl_2$  (0.13 g, 1 mmol) in  $CH_3OH$  was added to the green solution. The reaction temperature rose to r.t. by removing the cold bath and  $Et_4NCl$  (0.2 g, 1.2 mmol) was added. The mixture was stirred for another 24 h. After filtering off a small amount of solid, the dark red filtrate was pumped to dryness. The solid residue was dissolved in 15 ml of  $CH_3OH$  and then 7 ml of isopropane was added. After filtering off a little residue the final filtrate was cooled at  $4^\circ C$  for 2 weeks. A total of 0.42 g of crystalline dark red product  $[Et_4N]_2[MnFe_4S_4(CO)_{12}]$  (2) was collected. Yield: 41.9% (based on  $[Fe_2S_2(CO)_6]$  used). Elemental Anal. Calc. for  $C_{28}H_{40}N_2MnFe_4S_4O_{12}$ , C, 33.5; H, 4.0; N, 2.8; Fe, 22.3. Found: C, 33.0; H, 4.0; N, 2.5; Fe, 22.4%. IR (KBr pellet) 2044s, 2008s, 1981s and 1963s  $cm^{-1}$  ( $\nu_{CO}$ ).

#### 3.4. Synthesis of $[Et_4N]_2[CrFe_4S_4(CO)_{12}]$ (3)

A small amount of Zn powder was added to a solution of  $CrCl_3$  (0.11 g, 0.69 mmol) in 20 ml of THF resulting in a color change from violet to light green (part A).  $LiEt_3BH$ –THF (1 M, 1.5 ml) was dropped slowly into a solution of  $Fe_2S_2(CO)_6$  (0.25 g, 0.73 mmol) in 20 ml THF at  $-78^\circ C$  resulting in a color change from red to green. Part A was added to this resulting solution. After stirring at  $-78^\circ C$  for 0.5 h the reaction temperature was raised to r.t. by removing the cold bath.  $Et_4NBF_4$  (0.6 g, 2.76 mmol) was added and the reaction mixture was stirred at r.t. for another 24 h resulting in a red–brown solution. After filtering off a small amount of brown precipitate, the filtrate was pumped to dryness. The residue was dissolved in 15 ml of  $CH_2Cl_2$  and then 8 ml of hexane was added. After filtering, the filtrate was cooled at  $4^\circ C$  for 2 weeks. A

total of 0.1 g of the dark microcrystalline product  $[\text{Et}_4\text{N}]_2[\text{CrFe}_4\text{S}_4(\text{CO})_{12}]$  (**3**) was collected. Yield: 27.4% (based on  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  used). Anal. Calc. for  $\text{C}_{28}\text{H}_{40}\text{N}_2\text{CrFe}_4\text{S}_4\text{O}_{12}$ : Cr, 5.2; Fe, 22.3; C, 33.6; H, 4.0; N, 2.8. Found: Cr, 5.4; Fe, 22.1; C, 33.9; H, 3.8; N, 2.4%. IR (KBr pellet); 2044s, 2013s, 1975s and 1963  $\text{cm}^{-1}$  ( $\nu_{\text{CO}}$ ).

### 3.5. X-ray crystal structure determination

A dark crystal samples of compound **1** and **2** wrapped with glue were mounted on Siemens Smart CCD diffractometer equipped with a graphite monochromator (Mo-K $\alpha$  radiation  $\lambda = 0.71073 \text{ \AA}$ ) for data collection. The crystal data, collection and refinement details are listed in Table 4. All calculations were performed on a Silicon Graphics computer station by using the SHELXTL program system.

Data were corrected for Lorentz and polarization effects and for absorption effects by SADABS [24]. The

Table 4  
Crystal data and collection and refinement details for **1** and **2**

Compounds	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{12}\text{Fe}_4\text{O}_{12}\text{S}_4\text{V}$	$\text{C}_{84}\text{H}_{120}\text{Fe}_{12}\text{Mn}_3\text{N}_6\text{O}_{36}\text{S}_{12}$
Formula weight	738.70	3009.60
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (Å)	9.1418(3)	18.7335(5)
<i>b</i> (Å)	10.6431(3)	19.5615(3)
<i>c</i> (Å)	12.7824(3)	36.2523(7)
$\alpha$ (°)	100.0881(1)	90
$\beta$ (°)	92.850(1)	104.0020(10)
$\gamma$ (°)	109.764(1)	90
<i>V</i> (Å <sup>3</sup> )	1144	12890
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (mg cm <sup>-3</sup> )	2.144	1.551
$\lambda$ (mm <sup>-1</sup> )	3.289	1.851
Crystal size (mm <sup>3</sup> )	$0.6 \times 0.4 \times 0.4$	$0.6 \times 0.5 \times 0.45$
$\theta$ Range (°)	1.63–23.26	1.19–24.00
Index ranges	$-9 \leq h \leq 10,$ $-11 \leq k \leq 11,$ $-8 \leq l \leq 14$	$-21 \leq h \leq 20,$ $0 \leq k \leq 22,$ $0 \leq l \leq 41$
Reflections collected	4499	19 728 [ $R_{\text{int}} = 0.0000$ ]
Independent reflections	3168	19728
No. observations with $I > 2\sigma(I)$	2712	10516
Data/restraints/parameters	3168/0/299	19728/0/740
Goodness-of-fit	0.997	1.069
$R_1, wR_2$ ( $I > 2\sigma(I)$ )	0.0302, 0.0826	0.0873, 0.1657
$R_1, wR_2$ (all data)	0.0347, 0.0892	0.1633, 0.1979
Largest difference peak and hole (e Å <sup>-3</sup> )	0.702/–0.511	0.734/–0.359

structure was solved by directed methods (SHELXTL) and were refined by the full-matrix least-squares on all  $F^2$  data using Silicon Graphics Indy computer [25]

## 4. Summary

New mixed metal penta-nuclear clusters  $[\text{VFe}_4\text{S}_4(\text{CO})_{12}]$  (**1**),  $[\text{Et}_4\text{N}]_2[\text{MnFe}_4\text{S}_4(\text{CO})_{12}]$  (**2**) and  $[\text{Et}_4\text{N}]_2[\text{CrFe}_4\text{S}_4(\text{CO})_{12}]$  (**3**) have been synthesized by the reaction of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$  with  $\text{VCl}_3$ ,  $\text{MnCl}_2$  and  $\text{CrCl}_3 + \text{Zn}$ , respectively. Crystal structure determination shows that **1** contains a  $[\text{VFe}_4\text{S}_4]$  core with V–Fe bonds and **2** possesses a  $[\text{MnFe}_4\text{S}_4]^{2-}$  core without any Mn···Fe interaction. The  $[\text{Fe}_2\text{S}_2]$ -units in both **1** and **2** are in butterfly type. IR spectra studies indicate that IR spectra of **1**, **2** and **3** are very similar implying that **3** probably has the same structure as complex **2** does. Finally, the reaction pathway of the complexes have been discovered and discussed.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 197025 and 199963 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336066; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## References

- [1] W. Hieber, J. Gruber, Z. Anorg. Allg. Chem. 296 (1958) 91.
- [2] C.H. Wei, L.F. Dahl, Inorg. Chem. 4 (1965) 1.
- [3] D. Seyferth, R.S. Hederson, L.-C. Song, Organometallics 1 (1982) 123.
- [4] D. Seyferth, R.S. Hederson, J. Am. Chem. Soc. 101 (1979) 508.
- [5] D. Seyferth, R.S. Hederson, L.-C. Song, J. Organomet. Chem. 192 (1980) C1.
- [6] K.S. Bose, P.E. Lamberty, J.A. Kovacs, E. Sinn, B.A. Averill, Polyhedron 5 (1986) 393.
- [7] B. Zhuang, B. Pan, L. Huang, P. Yu, Inorg. Chim. Acta 227 (1994) 119.
- [8] P. Mathur, P. Sekar, Chem. Commun. (1996) 727.
- [9] B. Zhuang, P. Chen, L. Huang, J. Lu, Polyhedron 11 (1992) 127.
- [10] R.L. Holliday, L.C. Roof, B. Hargs, D.M. Smith, P.T. Wood, W.T. Pennington, J.W. Kolis, Inorg. Chem. 34 (1995) 4392.
- [11] D.E. Barber, M. Sabat, E. Sinn, B.A. Averill, Organometallics 14 (1995) 3229.
- [12] A.A. Pasynskii, I.L. Eremenko, A.S. Ablullaev, B. Orazsakhmetov, S.E. Nefedov, E.E. Stomakina, O.G. Ellert, S.B. Katsar, A.L. Yanovsky, Yu.T. Strouokov, Zh. Neorg. Khim. 35 (1990) 2257.
- [13] A.A. Pasynskii, B.I. Kolobkov, I.L. Eremenko, S.E. Nefedov, S.B. Katsar, M.A. Porai-Kashits, Zh. Neorg. Khim. 37 (1992) 563.
- [14] H. Zhu, Q. Liu, C. Chen, Chin. J. Struct. Chem. 20 (2001) 19.

- [15] (a) E.J. Baerends, D.E. Eills, P. Ros, *Chem. Phys.* 2 (1973) 41;  
(b) E.J. Baerends, *J. Comput. Phys.* 99 (1992) 84.
- [16] D. Seyferth, R.S. Henderson, J.P. Fackler Junior, A.M. Mazany, *J. Organomet. Chem.* 213 (1981) C21.
- [17] W.M. Scovell, T.G. Spiro, *Inorg. Chem.* 13 (1974) 304.
- [18] R.J. Kern, *J. Inorg. Nucl. Chem.* 24 (1962) 1105.
- [19] D. Seyferth, R.S. Henderson, M.K. Gallagher, *J. Organomet. Chem.* 193 (1980) C75.
- [20] P.A. Eldredge, R.F. Bryan, E. Sinn, B.A. Averill, *J. Am. Chem. Soc.* 110 (1988) 5573.
- [21] K.S. Bose, S.A. Chmielewski, P.A. Eldredge, E. Sinn, B.A. Averill, *J. Am. Chem. Soc.* 111 (1989) 8953.
- [22] P.A. Eldredge, K.S. Bose, D.E. Barber, B.A. Averill, *Inorg. Chem.* 30 (1991) 2365.
- [23] B. Zhuang, B. Pan, L. Huang, L. He, P. Cheng, H. Sun, G. Pan, *Chin. J. Struct. Chem.* 17 (1998) 35.
- [24] G.M. Sheldrick, *SADABS*, Absorption Correction Program, University of Göttingen, German, 1996.
- [25] G.M. Sheldrick, *SHELXTL* 5.03, Siemens Analytical X-ray Instrument Inc., Madison, WI, 1990.