CLUSTER SYNTHESIS—XXIII. THE SYNTHESIS, STRUCTURE AND BONDING OF $Fe_4(CO)_{10}(\mu-CO)(\mu_4-S)_2$

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(Received 15 December 1988; accepted 13 February 1989)

Abstract—The compound $Fe_4(CO)_{10}(\mu-CO)(\mu_4-S)_2$ (1) was synthesized in 38% yield by the UV induced decarbonylation of $Fe(CO)_5$ in the presence of $Fe_3(CO)_9(\mu_3-S)_2$. Compound 1 was characterized by a single-crystal X-ray diffraction analysis. Space group: *Pccn*, a = 6.603(1), b = 15.429(3), c = 17.292(4) Å, Z = 4. The structure was solved by direct methods and was refined (807 reflections) to the final values of the residuals R = 0.043 and $R_w = 0.054$. The molecule consists of a planar array of four iron atoms with a quadruply bridging sulphido ligand on each side of the plane. The shortest metal–metal bond, 2.489(3) Å, contains a bridging carbonyl ligand. Semi-bridging carbonyl ligands bridge the two adjacent metal–metal bonds, 2.532(2) Å. The longest metal–metal bond, 2.605(2) Å, has no carbonyl bridge. Compound 1 is unsaturated (by EAN rule) by the amount of two electrons. The two semi-bridged carbonyl–metal bonds in 1 are significantly shorter than those in the saturated cluster $Fe_2Co_2(CO)_{11}(\mu_4-S)_2$. A molecular orbital description which explains the differences in bonding between the two compounds is proposed.

Recently, we have demonstrated the value of Ru(CO)₅ and Os(CO)₅ as reagents for the enlargement of metal carbonyl clusters of ruthenium and osmium that contain sulphido ligands.¹⁻⁵ We have now begun investigations into the iron system. This report describes the synthesis and structural characterization of the new iron cluster, Fe₄(CO)₁₀(μ -CO)(μ ₄-S)₂ (1). The structure of compound 1 was compared with that of Fe₂Co₂(CO)₁₀(μ -CO) (μ -S)₂ (2), which has an analogous structure, but has two additional valence electrons.⁶ A molecular orbital description that explains differences in the metal-metal bonding of the two structures is proposed.

EXPERIMENTAL

General procedures

Compound 1 is slightly air-sensitive. Thus, all reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. Fe(CO)₅ was purchased from Alfa. Fe₃(CO)₉(μ_3 -S)₂ was prepared as previously reported.⁷ IR spectra were recorded on a Nicolet 5-DXB FT-IR spectrometer. Elemental analysis was performed by Desert Analytics, Tucson, Arizona.

Synthesis of $Fe_4(CO)_{10}(\mu$ -CO)(μ_4 -S)₂ (1)

 $Fe_3(CO)_9(\mu_3-S)_2$ (50 mg, 0.103 mmol) and $Fe(CO)_5$ (0.136 cm³, 1.03 mmol) were dissolved in 50 cm³

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of cyclohexane solvent in a Pyrex flask. The solution was irradiated (UV external) in the presence of a continuous nitrogen purge for 4.5 h. The solvent was removed *in vacuo* and the residue was chromatographed by TLC on silica gel with hexane solvent. This yielded the following compounds in order of elution : yellow Fe₂(CO)₆(S)₂, 3 mg; red Fe₃(CO)₉(μ_3 -S)₂, 21.8 mg, and green 1, 13.1 mg (38% based on the amount of Fe₃(CO)₉(μ_3 -S)₂ consumed). Found : C, 21.57. Calc : C, 22.18%. IR(ν CO in hexane) : 2063(w), 2044(s), 2022(m), 2011(m), 1856(w).

Reaction of 1 with carbon monoxide

15 mg of 1 were dissolved in 30 cm³ of hexane. The solution was refluxed under a slow purge of carbon monoxide for 18 h. During this time the green solution turned to a greenish-red colour. The solvent was then removed *in vacuo*, and the residue was chromatographed by TLC. This yielded (in order of elution): yellow $Fe_2(CO)_6(\mu$ -S₂) (0.5 mg), red $Fe_3(CO)_9(\mu_3$ -S)₂ (6.5 mg) and unreacted 1 (6.4 mg).

Molecular orbital calculations

Fenske-Hall molecular orbital calculations⁸ were performed on a VAX 11/780 computer. The iron basis functions were taken from Richardson *et al.*⁹ The carbon, oxygen and sulphur functions were taken from the double- ζ functions of Clementi¹⁰ and reduced to a single- ζ function, ¹¹ except for the *p*-valence functions which were retained as the double- ζ function. The atomic functions were made orthogonal by the Schmidt procedure. The Mulliken population analysis¹² was used to determine both the individual atomic charges and the atomic orbital populations.

Calculations were performed on 1 in its crystal structure geometry. Additional calculations were performed on 2 in its crystal structure geometry⁶* and the 2⁺ cation of 2 (hereafter designated as 2a), in order to compare the effect of adding two electrons to the fixed cluster framework. The calculations were performed with 3*d*-orbitals included on the capping sulphur atoms (exponents equal to that of the best atom single- ζ 3*p*-function).

Crystallographic analyses

Very dark green crystals of 1 suitable for X-ray diffraction measurements were grown by slow evap-

oration of solvent from solutions in a CH₂Cl₂- C_6H_{14} solvent mixture at 5°C. The data crystal was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer, using graphite monochromatized $Mo-K_{\pi}$ radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the diffractometer automatic search, centre, index and least-squares routines. Crystal data and results of the analysis are listed in Table 1. All data processing was performed on a Digital Equipment Corporation MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, College Station, Texas. Neutral atom scattering factors were calculated by the standard procedures.^{13a} Anomalous dispersion corrections were applied to all non-hydrogen atoms.^{13b} Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} \mathbf{w}(|F_{obs}| - |F_{calc}|)^2$$

where

and

 $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_{obs}^2)/2F_{obs}$

$$\sigma(F_{\rm obs}^2) = [\sigma(I_{\rm raw})^2 + (PF_{\rm obs}^2)^2]^{1/2}/Lp.$$

All non-hydrogen atoms were refined anisotropically. The unit cell and systematic absences indicated that the crystals belonged to the orthorhombic crystal system and the space group, *Pccn*. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses.

RESULTS AND DISCUSSION

When purged with nitrogen, solutions of $Fe_3(CO)_9(\mu_3-S)_2$ and $Fe(CO)_5$ exposed to UV irradiation yield the new compound $Fe_4(CO)_{10}(\mu$ -CO)(μ_4 -S)₂ (1) (38% yield based on the amount of $Fe_3(CO)_9(\mu_3-S)_2$ consumed in the reaction). When treated with carbon monoxide (1 atm) in refluxing hexane solvent (18 h), compound 1 was converted back to Fe₃(CO)₉(μ_3 -S)₂ (53% yield) by removal of one iron grouping, presumably as Fe(CO)₅. Compound 1 was characterized by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of 1 is shown in Fig. 1. Intramolecular bond distances and angles are listed in Tables 2 and 3. The molecule contains a C_2 rotation axis that is crystallographically imposed. The bridging ligand C(11)—O(11) lies on this axis. The cluster consists of a trapezoidal arrangement of four iron

^{*} Additional details concerning the structure of 2 were provided by Professor H. Vahrenkamp.

(a)	Formula	Fe ₄ S ₂ O ₁₁ C ₁₁
•	Temperature $(+3^{\circ}C)$	23
	Space group	Pccn
	a (Å)	6.603(1)
	$b(\mathbf{A})$	15.429(3)
	$c(\mathbf{A})$	17.292(4)
	$V(\mathbf{A}^3)$	1761 6(7)
	M	595.6
	7	A
	$a_{\rm c}$ (g cm ⁻³)	
(h)	Measurement of intensity data	2.23
(0)	Radiation	
	Monochromator	$M_{0} K (0.71060 \text{ Å})$
	Detector aparture (mm)	$MO-R_{\alpha} (0.71007 A)$
	Horizontal	2α
	Mor 20	2.0 45.0°
	Max 20	
	Scan type	Moving crystal-stationary counter
	ω -Scan width:	$A = 1.10^{\circ}$
	$(A+0.34/\tan\theta)^{\circ}$	1
	Background (count time at each end of scan):	additional scan
	ω -Scan rate" (° min ⁻¹)	4.0
	Data used $(F^2 \ge 3.0\sigma(F^2))$	807
	Data measured	1379
(c)	Treatment of data	
	Absorption correction:	Analytical
	Coefficient (cm^{-1}) :	35.1
	Transmission coefficient :	
	Maximum	0.83
	Minimum	0.46
	Number of variables	128
	Vertical	2.0
	Crystal faces:	010, 0 T 0, 00T
		011, 110, 110
	Crystal size (mm):	$0.08 \times 0.18 \times 0.24$
	Crystal orientation :	
	Direction; ° from ϕ -axis	<i>a</i> , <i>^{<i>a</i>} 3.5</i>
	Reflections measured	$+h_{1}+k_{2}+l_{3}$
	P-factor	0.02
	Final residuals $R_{\rm F}$	0.043
	R _{wE}	0.054
	Goodness-of-fit	1.87
	Largest shift-error	
	Value of final cycle	0.00
	Largest neak in final difference Fourier $(e^{-\Delta} - 3)$	0.70
	or of pour in man and only one found (C A)	0.70

Table 1. Crystallographic data for X-ray diffraction study

^a Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to the first scan, etc. A maximum of three scans was permitted per reflection.

atoms which is bridged on each side by a quadruply bridging sulphido ligand. It is structurally very similar to $Fe_2Co_2(CO)_{10}(\mu$ -CO)(μ_4 -S)₂ (2),⁶* and the structures of both compounds will be compared and contrasted. The shortest metal-metal bond in 1 contains a bridging carbonyl ligand, Fe(1)—Fe(1') = 2.489(3) Å. The corresponding

bond in 2 is the cobalt-cobalt bond, which is essentially equal in length, 2.495(2) Å. Fe(2)—Fe(2') is the longest metal-metal bond in 1, 2.605(2) Å, and compares favourably with the corresponding Fe—Fe bond in 2, 2.604(2) Å. The sides of the trapezoid in 1, Fe(1)—Fe(2), are equal in length, 2.532(2) Å, but are significantly shorter, 0.045-



Fig. 1. An ORTEP diagram of $Fe_4(CO)_{10}(\mu$ -CO) $(\mu_4$ -S)₂ (1) showing 50% probability thermal ellipsoids.

0.048 Å, than the corresponding bonds in 2, Fe-Co, 2.580(2) and 2.577(2) Å.⁹ In both 1 and 2, these metal-metal bonds contain semi-bridging carbonyl ligands, but the semi-bridging effect is slightly stronger in 1, Fe(2)-C(21)-O(21) = $161.2(8)^{\circ}$, than in 2, Fe—C—O = 167(1) and 169(1)°. The metal-sulphur bonds in 1 and 2 are very similar, Fe(1)—S = 2.332(2) Å, Fe(1')—S = 2.347(2) Å, Fe(2)—S = 2.278(2) Å and Fe(2')—S = 2.294(2) Å in 1, and Fe—S = 2.262(3)-2.277(2) Å and Co-S = 2.303(2)-2.329(2) Å in 2. The non-bonding $S \cdots S'$ distance in 1 is 2.911(4) Å.

One of the products obtained from the reaction of Ru(CO)₅ with Ru₃(CO)₉(μ_3 -S)₂ was Ru₄(CO)₉(μ -CO)₂(μ_4 -S)₂.⁴ The structure of this compound was determined in the form of the bisphosphine substituted derivative, Ru₄(CO)₇(PMe₂ Ph)₂(μ -CO)₂(μ ₄-S)₂ (3). The cluster of 3 is similar to that of 1 and 2, but 3 contains two bridging carbonyl ligands. The Ru—Ru bonds associated with the bridging carbonyl ligands are significantly shorter than the unbridged Ru—Ru bonds.

Compound 1 contains a total of 62 valence electrons. According to the Effective Atomic Number (EAN) rule, it is electron deficient by two electrons, although it does obey the Skeletal Electron Pair (SEP) theory.¹⁴ Compound 2 on the other hand, contains 64 valence electrons and obeys the EAN rule. It was of interest to examine the possibility that the comparative shortness of the Fe(1)—Fe(2) bonds in 1 could be related to its intrinsic unsaturation. These results are described in the following section and are compared with those of Halet *et al.*, who investigated the cluster bonding in the molecules $M_4(CO)_n(\mu_4-L)_2$ (n = 11, 12) by the extended Hückel method.¹⁵

In Fig. 2 is shown the coordinate systems used in the calculations. In the coordinate systems about the iron atoms, the z-axis points towards the centre of the Fe_4 trapezoid, the y-axis is tangential to the trapezoid and the x-axis is perpendicular to the Fe_4 plane. The HOMO of compound 1 is primarily of Fe x^2-y^2 character of all four iron atoms with the major portion on the unbridged Fe(2) and Fe(4) atoms (13.5% Fe(2) and Fe(4) x^2-y^2 vs 2.8% Fe(1) and Fe(3) x^2-y^2). It possesses a node through the semi-bridged Fe(1)—Fe(2) and Fe(3)—Fe(4) bonds. The LUMO, 1.88 eV above the HOMO, is very similar to the HOMO of b_u symmetry in Halet's calculations on the cluster $Fe_4(CO)_{12}(\mu-PH)_2$ (4), which contains two more electrons.¹⁵ This orbital is mainly of Fe xz character on all the iron atoms and is antibonding around the Fe₄ ring. It contains slightly more xz character on the bridged Fe(1) and Fe(3) atoms than on the unbridged Fe(2) and Fe(4)atoms (12.3 vs 7.5%). In his calculations on 4, Halet¹⁵ noted that the HOMO would be stabilized

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Fe(1)	C(12)	1.77(1)	Fe(2)	S	2.278(2)
Fe(1)	C(13)	1.79(1)	Fe(2')	S	2.294(2)
Fe(1)	C(11)	1.93(1)	Fe(2)	Fe(2')	2.605(2)
Fe(1)	S	2.332(2)	O(11)	C(11)	1.15(2)
Fe(1')	S	2.347(2)	O(12)	C(12)	1.14(1)
Fe(1)	Fe(1')	2.489(3)	O(13)	C(13)	1.12(1)
Fe(1)	Fe(2)	2.532(2)	O(21)	C(21)	1.16(1)
Fe(2)	C(23)	1.76(1)	O(22)	C(22)	1.14(1)
Fe(2)	C(22)	1.77(1)	O(23)	C(23)	1.14(1)
Fe(2)	C(21)	1.79(1)	S	S	2.911(4)

Table 2. Intramolecular distances for $Fe_4(CO)_{10}(\mu-CO)(\mu_4-S)_2$ (1)

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C(12)	Fe(1)	C(13)	90.6(4)	C(23)	Fe(2)	Fe(2')	104.3(3)
C(12)	Fe(1)	C(11)	92.0(4)	C(22)	Fe(2)	C(21)	94.8(4)
C(12)	Fe(1)	S	94.1(3)	C(22)	Fe(2)	S'	92.4(3)
C(12)	Fe(1)	S′	169.1(3)	C(22)	Fe(2)	S	158.2(3)
C(12)	Fe(1)	Fe(1')	123.0(3)	C(22)	Fe(2)	Fe(1)	133.6(3)
C(12)	Fe(1)	Fe(2)	114.2(3)	C(22)	Fe(2)	Fe(2')	103.7(3)
C(13)	Fe(1)	C(11)	90.6(3)	C(21)	Fe(2)	S	104.1(3)
C(13)	Fe(1)	S	172.0(3)	C(21)	Fe(2)	S	106.7(3)
C(13)	Fe(1)	S	97.5(3)	C(21)	Fe(2)	Fe(1)	63.8(3)
C(13)	Fe(1)	Fe(1')	123.8(3)	C(21)	Fe(2)	Fe(2')	152.4(3)
C(13)	Fe(1)	Fe(2)	116.0(3)	S	Fe(2)	S'	79.1(1)
C(11)	Fe(1)	S	95.7(2)	S	Fe(2)	Fe(1)	58.11(7)
C(11)	Fe(1)	S′	95.2(2)	S	Fe(2)	Fe(2')	55.55(7)
C(11)	Fe(1)	Fe(1')	49.8(3)	S	Fe(2)	Fe(1)	57.53(6)
C(11)	Fe(1)	Fe(2)	141.1(3)	S	Fe(2)	Fe(2')	54.99(6)
S	Fe(1)	S′	77.0(1)	Fe(1)	Fe(2)	Fe(2')	88.69(4)
S	Fe(1)	Fe(1')	58.15(7)	Fe(2)	S	Fe(2')	69.46(8)
S	Fe(1)	Fe(2)	56.09(6)	Fe(2)	S	Fe(1')	102.31(9)
S′	Fe(1)	Fe(1')	57.56(7)	Fe(2)	S	Fe(1)	66.36(7)
S′	Fe(1)	Fe(2)	55.52(6)	Fe(2')	S	Fe(1')	66.37(7)
Fe(1')	Fe(1)	Fe(2)	91.30(4)	Fe(2')	S	Fe(1)	101.39(9)
C(23)	Fe(2)	C(22)	89.1(4)	Fe(1)	S	Fe(1')	64.29(8)
C(23)	Fe(2)	C(21)	96.1(4)	O(11)	C(11)	Fe(1)	139.8(3)
C(23)	Fe(2)	S'	159.6(3)	O(11)	C(11)	Fe(1')	139.8(3)
C(23)	Fe(2)	S	92.1(3)	Fe(1)	C(11)	Fe(1')	80.4(6)
C(23)	Fe(2)	Fe(1)	131.4(4)	O(12)	C(12)	Fe(1)	178(1)
O(13)	C(13)	Fe(1)	177.3(8)		. ,		
O(21)	C(21)	Fe(2)	161.2(8)				
O(22)	C(22)	Fe(2)	179(1)				
O(23)	C(23)	Fe(2)	179(1)				

Table 3. Intramolecular bond angles for $Fe_4(CO)_{10}(\mu-CO)(\mu_4-S)_2$ (1)

in the calculations by the addition of *d*-orbitals on the capping phosphorus atom and indeed this is the case for 1. Our LUMO contains a substantial amount of sulphur xy character (7.5%) from each capping sulphur atom.

The calculation on compounds 2 and 2a (the 2^+ cation of 2) gave similar orbitals for the HOMO



Fig. 2. Molecular and local coordinate systems used in Fenske-Hall calculations on compound 1.

and LUMO of 2a and the SHOMO and HOMO of 2, respectively. The HOMO-LUMO gap has shrunk considerably to 0.13 eV for 2a. Comparing the overlap population between the metal atoms for the three types of metal-metal bonds in the cluster, one can observe the effect of adding two electrons to the M_4 framework. The overlap populations are shown in Table 4. As two electrons are added to 2a to form 2, the overlap populations for all three types of metal-metal bonds decrease in value. This is not too surprising since the LUMO of 2a is antibonding along each metal-metal bond axis. However, the total overlap goes from bonding to antibonding for the semi-bridged Fe-Co bond and the bridged Co---Co bond. The largest decrease in overlap population (0.038) occurs for the bridged Co-Co bond. However, the metal atoms could be restrained from moving further apart by the bridging carbonyl ligand. The semi-bridged Fe-Co bonds show a decrease in overlap of 0.026 upon the addition of two electrons. Since semi-bridging ligands are presumably not as supportive as a full bridge, the Fe-Co bonds might be lengthened as a result. The

Table 4. Mulliken overlap populations along the metalmetal bonds of $[Fe_2M_2(CO)_{10}(\mu-CO)(\mu_4-S)_2]$ (M = Fe or Co)

Compound	Fe—Fe unbridged	Fe—M semi-bridged	M—M bridged
1 (M = Fe)	0.036	0.016	0.018
2(M = Co)	0.026	0.017	0.013
2a (M = Co)	0.016	-0.009	-0.025

unbridged Fe—Fe bond shows the smallest decrease in overlap population (0.010) and the overlap is positive for 1, 2 and 2a. Thus, bond lengthening effects might remain small on the Fe—Fe bond. We expect that the structural differences between 1 and 2 would be similar to those between 2a and 2. This is fully consistent with our observations.

Acknowledgements—This research was supported by the National Science Foundation under Grant No. CHE-8612862 to R.D.A. and by the Robert A. Welch Foundation under Grant No. A-648 to M.B.H. Funds to purchase the VAX 11/780 at Texas A&M University were provided by the National Science Foundation. We wish to thank Professor H. Vahrenkamp for providing us with additional details concerning the structure of **2**.

Supplementary material. Atomic coordinates have been deposited with the Director, Cambridge Crystallographic Data Centre.

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