

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ DIANION: A MODEL COMPOUND FOR AN ADSORBED OXYGEN ATOM

A. CERIOTTI, L. RESCONI

Dipartimento di Chimica Inorganica e Metallorganica, via Venezian 21, 20133 Milano (Italy)

F. DEMARTIN, G. LONGONI, M. MANASSERO, and M. SANSONI

Centro del C.N.R. per la Sintesi e la Struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, via Venezian 21, 20133 Milano (Italy)

(Received March 21st, 1983)

Summary

The reaction of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ with oxygen gives an almost quantitative yield of the new red-orange $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ dianion, which has been isolated in a crystalline state as the trimethylbenzylammonium salt and characterized by an X-ray study. This new cluster may be regarded as model for an oxygen atom adsorbed on a metal surface.

The chemistry of metal carbonyl clusters containing exposed or semi-exposed main group elements such as carbon or nitrogen, as well as small polyatomic fragments derived from them, has received increasing interest in recent years [1–4]; largely as a consequence of the belief that such molecular clusters may provide the most reliable model for the interaction and chemical behaviour of corresponding species adsorbed on a metal surface [5].

Although a low-valent metal cluster* containing an exposed oxygen atom, $\text{Co}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-CO})(\mu_3\text{-O})$, was isolated and structurally characterized several years ago [7], to our knowledge only two other examples of this kind of clusters have been reported, viz. $[\text{Re}_3(\text{CO})_9(\mu_2\text{-H})_3(\mu_3\text{-O})]^{2-}$ [8] and the raft-like $\text{Os}_6(\text{CO})_{15}(\mu_3\text{-O})[\text{P}(\text{OCH}_3)_3]_4$ [9]. We report here the synthesis and structural characterization of an other member of this class of compound, the $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ dianion, which, in contrast to those mentioned above is readily and quantitatively available.

The $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ dianion was initially obtained by short exposure to

*High-valent metal cluster oxides or polynuclear compounds are common [6].

air of solutions of the red-violet $[\text{Fe}_3(\text{CO})_{11}]^-$ radical anion [10] during an attempt to isolate the latter in a crystalline state. Later we found that the dianion was more readily and conveniently produced by exposure to air of solutions of the parent $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ dianion, according to reaction 1. IR monitoring of the reaction showed formation of trace amounts $\text{Fe}(\text{CO})_5$ and $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$ as the

$$[\text{Fe}_3(\text{CO})_{11}]^{2-} + \text{O}_2 \rightarrow [\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-} + \text{CO}_2 + \text{CO} \quad (1)$$

only by-products. Concomitant formation of CO_2 was confirmed by GLC analysis of the gas phase when using carbon dioxide-free air. The resulting red-orange $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ dianion ($\nu(\text{CO})$ in THF at 2000w, 1935s, 1905m, 1875mw cm^{-1}) was isolated in the solid state as trimethylbenzylammonium salt in ca. 90% yield, and crystallized from tetrahydrofuran/cyclohexane by slow diffusion. (Calcd.: $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+$, 40.78; Fe, 22.78; CO, 34.26%; $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+/\text{Fe} = 1/1.5$. Found: $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+$, 40.1; Fe, 22.7; $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+/\text{Fe} = 1/1.52$.)

The correct stoichiometry and crystal structure were established by a single crystal X-ray study.

Crystal data: $\text{C}_{29}\text{H}_{32}\text{Fe}_3\text{N}_2\text{O}_{10}$, $M = 736.13$, monoclinic, space group $P2_1/n$, a 11.819(1), b 11.402(3), c 24.271(3) Å, β 93.94(2)°, V 3263 Å³, D_c 1.498 g cm⁻³ for $Z = 4$, $\mu(\text{Mo-K}\alpha)$ 13.7 cm⁻¹.

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo- K_α radiation (λ 0.71073 Å) in the θ range 3–25°. The structure was solved by conventional Patterson and Fourier methods and the

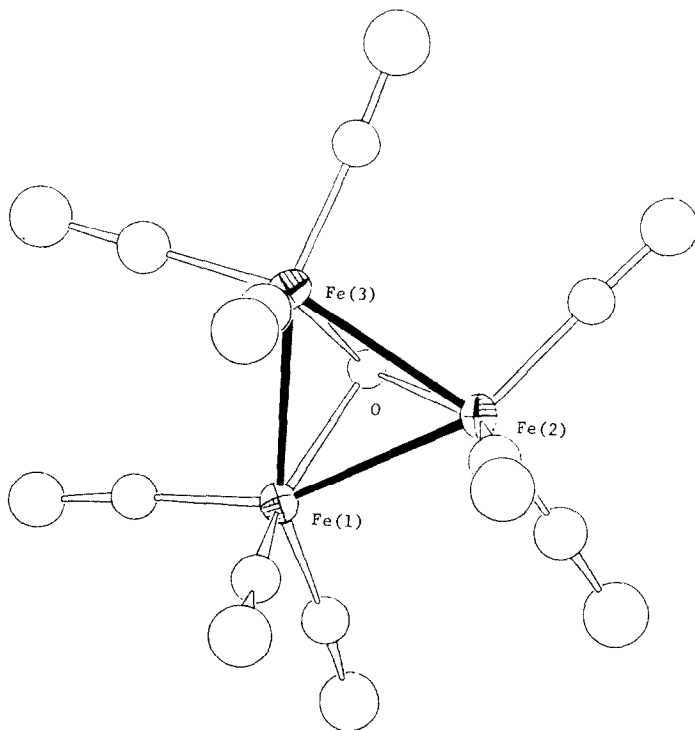


Fig. 1. Structure of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$. Bond lengths (Å): Fe(1)—Fe(2) 2.480(1), Fe(1)—Fe(3) 2.492(1), Fe(2)—Fe(3) 2.480(1), Fe(1)—O 1.895(3), Fe(2)—O 1.891(3), Fe(3)—O 1.890(3); Fe—C_{av} 1.771, C—O_{av} 1.152.

refinement carried out by full-matrix least-squares using 1798 independent absorption-corrected reflections having $I \geq 3\sigma(I)$, led to current R and R_w values of 0.041 and 0.051, respectively. Typical e.s.d.'s on single distances are: Fe—Fe 0.001, Fe—C 0.007, Fe—O 0.003, C—O 0.007 Å.

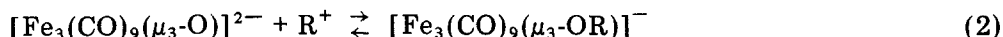
The structure derives from the packing of $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+$ cations and $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ dianions; a perspective view of the latter is given in Fig. 1, the legend to which presents the most significant molecular parameters.

The cluster of idealized C_{3v} symmetry is made up of an almost perfectly equilateral triangle of iron atoms. Each iron atom is bonded to three terminal carbonyl ligands. A unique oxygen atom sits on the top of the Fe_3 triangle and shows essentially equivalent interatomic separations from the three iron atoms (see Figure caption). Through the contribution of four valence electrons from the triply-bridging oxygen atom the dianion achieves a closed shell configuration.

The average Fe—Fe bond distance (2.484 Å) is shorter than in the parent $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ dianion (2.596 Å) [11], whereas it is comparable with the nitrogen-bridged Fe—Fe bond distances in $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NR})_2$ (2.462 Å) [12]. This feature is in keeping with previous finding that M—M interactions in ligand-bridged clusters are mainly affected by the size and effective electronegativity of the bridging atom [13,14].

The calculated covalent radius of the oxygen atom in $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ (0.65 Å) is close to that in $[\text{Re}_3(\text{CO})_9(\mu_2\text{-H})_3(\mu_3\text{-O})]^{2-}$ [8] (0.64 Å).

The residual nucleophilicity of the oxygen atom of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-O})]^{2-}$ is shown by the ready reaction with acids and alkyl halides (eq. 2). The resulting red-orange hydroxy- and alkoxy-derivatives have infrared spectra identical in



(R = H, CH_3 , $\text{CH}_2\text{CH}=\text{CH}_2$)

pattern to that of the parent dianion, but shifted ca. 30 cm^{-1} to higher frequencies. Their formulation is based on their spectra and chemical behaviour.

Similar reactivity is shown by the structurally related $[\text{Re}_3(\text{CO})_9(\mu_2\text{-H})_3(\mu_3\text{-O})]^{2-}$ [15].

References

- 1 M. Tachikawa and E.L. Muetterties, *J. Am. Chem. Soc.*, **102** (1980) 4541.
- 2 J.W. Kolis, E.M. Holt, M. Drezdzen, K.H. Whitmire and D.F. Shriver, *J. Am. Chem. Soc.*, **104** (1982) 6134.
- 3 J.S. Bradley, *Phil. Trans. R. Soc. London*, **A 308** (1982) 103.
- 4 M. Tachikawa, J. Stein, E.L. Muetterties, R.G. Teller, M.A. Beno, E. Gebert and J.M. Williams, *J. Am. Chem. Soc.*, **102** (1980) 6648.
- 5 E.L. Muetterties and J. Stein, *Chem. Rev.*, **79** (1979) 479.
- 6 E.L. Muetterties, *Chem. Eng. News*, **28**, Aug. 30, 1982.
- 7 V.A. Uchtman and L.F. Dahl, *J. Am. Chem. Soc.*, **91** (1969) 3763.
- 8 A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, *J. Organomet. Chem.*, **113** (1976) C61.
- 9 B.F.G. Johnson, *Phil. Trans. R. Soc. London*, **A 308** (1982) 5.
- 10 P.J. Kruzic, J. San Filippo, B. Hutchinson, R.L. Hance and L.M. Daniels, *J. Am. Chem. Soc.*, **103** (1981) 2129.
- 11 F. Yip-Kwai Lo, G. Longoni, P. Chini, L.D. Lower and L.F. Dahl, *J. Am. Chem. Soc.*, **102** (1980) 7691.
- 12 R.S. Doedens, *Inorg. Chem.*, **8** (1969) 570.
- 13 L.F. Dahl, E.R. de Gil and R.D. Feltham, *J. Am. Chem. Soc.*, **91** (1969) 1653.
- 14 L.F. Dahl, W.R. Costello and R.B. King, *J. Am. Chem. Soc.*, **90** (1968) 5422.
- 15 G. D'Alfonso, personal communication.