Crystal and Molecular Structure of $[Fe_4(CO)_{11}(NEt)(ONEt)]$: a New *Quadro* Iron Cluster with Two Face-bridging Organic Ligands

By Giuliana Gervasio,* Rosanna Rossetti, and Pier Luigi Stanghellini
(*Istituto di Chimica Generale ed Inorganica dell'Università, Corso Massimo D'Azeglio* 48, *Torino* 10125, *Italy*)

Summary *X*-Ray study of $[Fe_4(CO)_{11}(NEt)(ONEt)]$, obtained by the reaction of $[Fe_3(CO)_{12}]$ with nitroethane, has revealed the presence of a slightly distorted tetrairon square cluster with two organic ligands face-bridging the cluster, with eight terminal, two asymmetrical, and one symmetrical bridging carbonyl groups.

DURING an investigation of the reaction of $[Fe_3(CO)_{12}]$ with nitroethane, a product characterized as $[Fe_4(CO)_{11}(NEt)(ONEt)]$ was obtained in very low yield.[1] Its mass spectrum exhibits the molecular ion at m/e 634 and a fragmentation pattern indicating the loss of the 11 CO groups and the *N*-bonded oxygen atom. The 100 MHz ^1H n.m.r. spectrum ($CDCl_3$) shows signals at τ 9·68 (Me) and 8·27 (CH_2) assigned to the *N*-ethyl group, and at 9·19 (Me) and 6·41 (CH_2) assigned to the *ON*-ethyl group. The i.r. spectrum shows absorptions due to CO stretching frequencies at 2053s, 2033vs, 2028vs, 2012m, 1998s, 1993m sh (terminal CO's), and 1867m sh and 1845m (bridging CO's) cm^{-1}.

The complex crystallizes from n-heptane at −20 °C as deep-green crystals of the triclinic system, $M = 633·44$, space group $P\bar{1}$, with $a = 14·079(5)$, $b = 9·461(4)$, $c = 8·770(4)$ Å, $\alpha = 112·74(4)$, $\beta = 91·62(1)$, $\gamma = 92·05(1)°$, $U = 1075·5$ Å^3, $D_m = 1·97$, $D_c = 1·96$ g cm^{-3}, $Z = 2$.†

The reflection intensities were recorded with θ-2θ scanning on a Philips PW 1100 four-circle automatic diffractometer (Mo-K_α graphite monochromatized radiation, $\lambda = 0·7107$ Å). The initial Patterson synthesis and subsequent Fourier-difference maps revealed the heavy atom and all the non-hydrogen atom positions. Isotropic refinement by least-squares method led to the present $R = 0·081$, for 2249 observed reflections with $\theta < 30°$.

The molecule, shown in the Figure, contains a tetrairon nearly-planar cluster with four Fe–Fe bond distances along the sides of a slightly distorted square. Two carbonyl groups (not on the cluster plane) are bonded to each iron atom; of the remaining three carbonyls, two are asymmetrically bridged to Fe(1)–Fe(4) and Fe(2)–Fe(3) and the third symmetrically to Fe(3)–Fe(4).

On one face of the cluster the ethylamino-group is bridged, through the nitrogen atom, to the four iron atoms, while on the opposite face, the ONEt group is co-ordinated to Fe(1) and Fe(4) through the oxygen atom and to Fe(2) and Fe(3) through the nitrogen atom. This structure therefore has many interesting new features, including the rarely found[2] tetrametal planar cluster and the unusual bridge of an oxygen atom between two metals.[3] The presence of a pentaco-ordinated nitrogen atom must also be emphasized, even if an M.O. scheme would consider only four valence-orbitals in the bonding of the nitrogen atom to the ethyl group and to the four iron atoms.

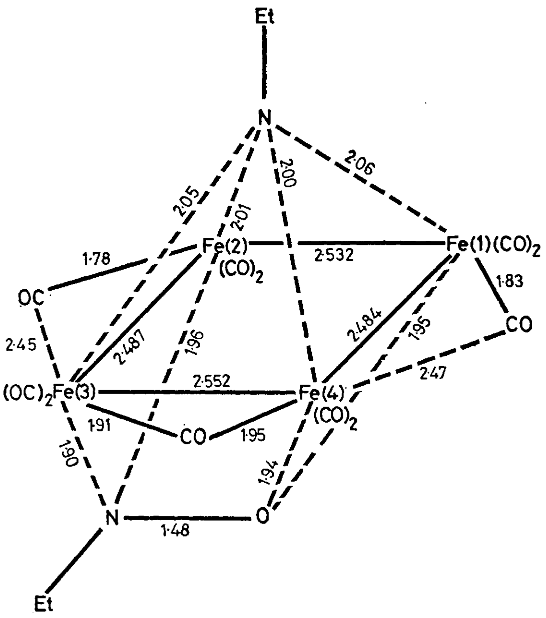

FIGURE. The structure of $[Fe_4(CO)_{11}(NEt)(ONEt)]$. Average e.s.d.s are: Fe–Fe, 0·004; Fe–N, 0·02; Fe–O, 0·01; and N–O, 0·02 Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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[3] R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.