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The Structure of μ-Diphenylureylene-bis(tricarbonyliron)

By J. A. J. JARVIS, B. E. JOB, B. T. KILBOURN, R. H. B. MAIS, P. G. OWSTON,* and P. F. TODD

(Petrochemical and Polymer Laboratory, Imperial Chemical Industries Ltd., P.O. Box 11, The Heath, Runcorn, Cheshire)

MANUEL[1] isolated a product from the reaction of tri-iron dodecacarbonyl and phenyl isocyanate which he formulated as $(C_6H_5NCO)_2Fe_2(CO)_6$. The structures[1,2] assigned to this complex appeared unusual and we decided to examine the compound by X-ray methods.

On repeating the preparation we were unable to confirm Manuel's formulation, although our compound appeared from its physical and chemical properties to be the same. Our compound analysed correctly for $(C_6H_5N)_2Fe_2(CO)_7$ and mass spectroscopy was used to confirm this. We named the compound μ-diphenylureylene-bis-(tricarbonyliron).[3] A family of parent ion-peaks was observed and the isotopic distribution around the principal ion at m/e 490 was indicative of a material containing two iron atoms; precise mass measurements confirmed the formula $C_{19}H_{10}N_2O_7Fe_2$. The cracking pattern was characteristic of a complex of the class [ligand] $Fe_2(CO)_6$,[4] with the elimination of six carbonyl groups—this was followed by the elimination of C_6H_5NCO from the $[P-6CO]^+$ ion to leave a $[C_6H_5NFe_2]^+$ fragment.

About this time Flannigan et al.,[5] published the results of their study of this compound and suggested the structure (I). We now confirm this structure from our own investigations.

The complex $C_{19}H_{10}N_2O_7Fe_2$ crystallizes in the monoclinic system, space group $P2_1/c$, $a = 8.51$, $b = 13.29$, $c = 19.51$ Å, $\beta = 106.6°$, $U = 2113$ Å,[3] $D_m = 1.55$, $Z = 4$, $D_c = 1.54$. A total of 2717 independent reflections with amplitudes

greater than 4 electrons were recorded on a Picker automatic diffractometer. The structure was solved by standard procedures and, after least-squares refinement with anisotropic temperature factors for the iron atoms and isotropic temperature factors for the remaining atoms, the R value is now 7.1% (hydrogens excluded). A difference map showed no significant residual electron density other than that attributable to hydrogen atoms. Standard deviations in bond distance are Fe–Fe, 0.002, Fe–light atom, 0.009, and light atom–light atom, 0.013 Å.

(I)
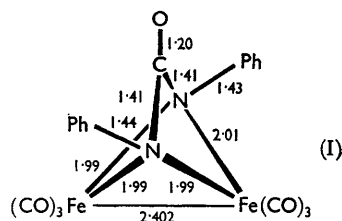
The two $Fe(CO)_3$ groups are bridged by both nitrogens, and the complex thus resembles μ-NN'-dehydrosemidinato-bis(tricarbonyliron),[6] and di-μ-(4,4'-dimethylbenzophenoniminato)-bis-(tricarbonyl iron).[7] The Fe–Fe distance in the latter complex, 2.403 Å, is the same as in the present structure. In the o-semidine complex[6] this distance is shorter, 2.37 Å. A similar variation of the Fe–Fe distance [between two $Fe(CO)_3$ groups] with slight changes in the bridging

ligands has been observed when two sulphurs are the bridging atoms.[8]

Certain angles in the present complex are Fe–N–Fe 74°, N–Fe–N 65°, Fe–Fe–N 53°, and N–C–N 98°. The angle N–C–N is much less than expected at sp^2 hybridized carbon. It seems difficult to reconcile this with the normal belief that it is the nature of the bridging group that determines the molecular geometry of such complexes.

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[6] P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, 1967, **1**, 55.
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