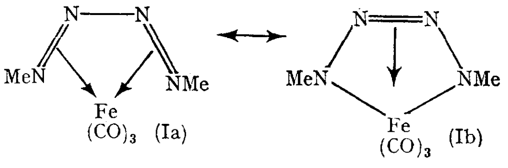
Molecular Configuration of $(Me)_2N_4Fe(CO)_3$, a Tetrazadiene–Tricarbonyliron Complex

By ROBERT J. DOEDENS

(*Department of Chemistry, University of California, Irvine, California* 92664)

THE most unusual product of the reaction of methyl azide with enneacarbonyldi-iron[1] is a volatile stable orange-red solid, $Me_2N_4Fe(CO)_3$. On the basis of i.r., n.m.r., and mass spectral data, a molecular structure (I) analogous to that of butadienetricarbonyliron was suggested by Dekker and Knox for this compound. A single-crystal *X*-ray structural analysis has now shown that the Me_2N_4 ligand is bound in a chelating fashion, resulting in a nearly planar $Fe–N_4$ ring. This is the first example of a metal complex of a tetrazadiene, RN_4R.

Crystals of $Me_2N_4Fe(CO)_3$ (supplied by Dr. G. R. Knox) are orthorhombic, $Z = 8$, $a = 22{\cdot}00$, $b = 12{\cdot}29$, and $c = 6{\cdot}64$ Å. The systematic absences, $h \neq 2n$ for $h0l$ reflections and $k \neq 2n$ for $hk0$ reflections, are consistent with space groups $P2_1ab$ (no.29) and $Pmab$ (no.57). A three-dimensional Patterson map could only be interpreted in terms of the former, noncentrosymmetric space-group and thus the asymmetric unit contains two crystallographically independent molecules. Intensity data for reciprocal lattice levels $hk0$–5 were collected by the multiple-film equi-inclination Weissenberg technique. The structure was solved by Patterson and Fourier methods, and an isotropic full-matrix least-squares refinement led to a final R of 6·2% for the 336 independent non-zero reflections. Owing to the low value of the data : parameter ratio and the marginal quality of the crystals, this structure is one of relatively low precision, with a standard deviation of 0·07 Å for bond lengths between light atoms. Hence, only average bond lengths of a given type will be discussed.



The monomeric $Me_2N_4Fe(CO)_3$ molecule (see Figure) consists of an $Fe(CO)_3$ group co-ordinated *via* a 1,4-linkage to the 1,4-dimethyltetrazadiene moiety, a species not known to exist as a free compound. Representations (Ia) and (Ib) for the bonding of this complex are inconsistent with the near-planarity of the five-membered ring and the fact that N(2) and N(3) are more than 2·6 Å away from the iron atom. If the N–Fe bonds are regarded as two-electron dative bonds, the iron atom attains its preferred 36-electron closed-shell configuration. It is reasonable that back-donation from the iron d_π orbitals to the π-antibonding orbitals of the tetrazadiene ligand could then serve to relieve the metal atom of an excess of negative charge. This model would imply a Fe–N bond order greater than one, which is consistent with the mean observed Fe–N bond length of 1·83 ± 0·03 Å. In a variety of related compounds,[2] the lengths of unequivocal Fe–N single bonds range from 1·95 to 2·02 Å. The observed mean Fe–N distance is thus closer to the length of a typical Fe–CO bond, in which the presence of multiple-bond character is generally accepted, than to that of an Fe–N single bond. The N–N bonds average 1·32 ± 0·03 Å in length, again a value indicative of the expected multiple-bond character in these bonds. The mean Fe–C, C–O, and C–N distances are 1·76 ± 0·03, 1·18 ± 03, and 1·53 ± 0·03 Å, respectively; all unremarkable values. None of the angles about the iron atom is within 20° of being linear, and the co-ordination seems best described as distorted square pyramidal.

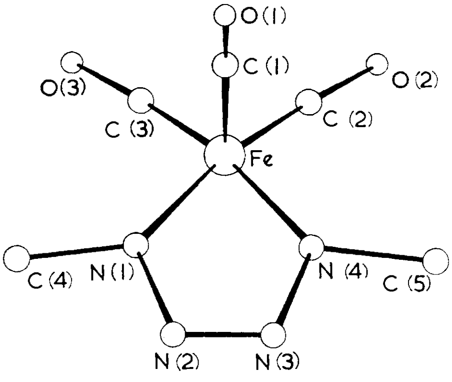


FIGURE. *The molecular configuration of* $Me_2N_4Fe(CO)_3$

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