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Molecular Configuration of $(\text{Me})_2\text{N}_4\text{Fe}(\text{CO})_3$, a Tetrazadiene-Tricarbonyliron Complex

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THE most unusual product of the reaction of methyl azide with enneacarbonyl-di-iron¹ is a volatile stable orange-red solid, $\text{Me}_2\text{N}_4\text{Fe}(\text{CO})_3$. On the basis of i.r., n.m.r., and mass spectral data, a molecular structure (I) analogous to that of butadienetetracarbyliron 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-N₄ ring. This is the first example of a metal complex of a tetrazadiene, RN_4R .

Crystals of $\text{Me}_2\text{N}_4\text{Fe}(\text{CO})_3$ (supplied by Dr. G. R. Knox) are orthorhombic, $Z = 8$, $a = 22.00$, $b = 12.29$, and $c = 6.64$ 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 $\text{Me}_2\text{N}_4\text{Fe}(\text{CO})_3$ molecule (see Figure) consists of an $\text{Fe}(\text{CO})_3$ 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

FIGURE. The molecular configuration of $\text{Me}_2\text{N}_4\text{Fe}(\text{CO})_3$

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 ± 0.03 , 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.

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