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Doedens, Robert J

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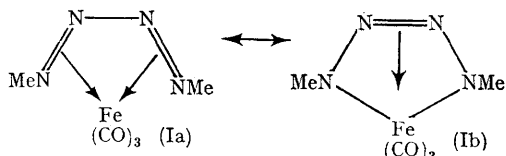
## Molecular Configuration of $(\text{Me})_2\text{N}_4\text{Fe}(\text{CO})_3$ , a Tetrazadiene-Tricarbonyliron Complex

By ROBERT J. DOEDENS

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

THE most unusual product of the reaction of methyl azide with enneacarbonyl-di-iron<sup>1</sup> 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 butadienetricarbonyliron was suggested by Dekker and Knox for this compound. A single-crystal X-ray structural analysis has now shown that the  $\text{Me}_2\text{N}_4$  ligand is bound in a chelating fashion, resulting in a nearly planar Fe-N<sub>4</sub> ring. This is the first example of a metal complex of a tetrazadiene,  $\text{RN}_4\text{R}$ .

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  $h \neq 2n$  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  $d_\pi$  orbitals to the  $\pi$ -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  $1.83 \pm 0.03$  Å. In a variety of related compounds,<sup>2</sup> the lengths of unequivocal Fe-N single bonds range from 1.95 to 2.02 Å. The observed mean Fe-N

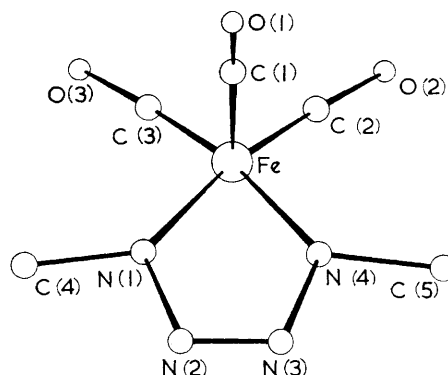


FIGURE. The molecular configuration of  $\text{Me}_2\text{N}_4\text{Fe}(\text{CO})_3$

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  $1.32 \pm 0.03$  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  $1.76 \pm 0.03$ ,  $1.18 \pm 0.03$ , and  $1.53 \pm 0.03$  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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