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K.J. Brewer, M. Richter, and B. Scott

July 1990

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Structure and Properties of a Bimetallic
Complex with a Conjugated Bridge between
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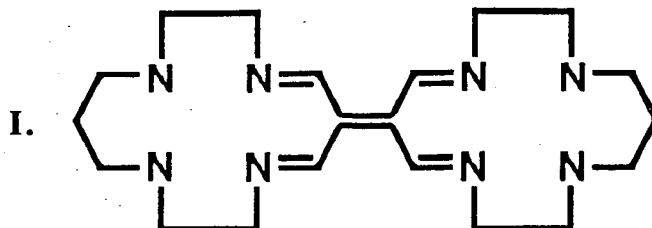
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the Associated Western Universities for support of HSM and LOS.

We have synthesized and isolated a bimetallic compound that is unique in that it contains a conjugated bridge between metals in two macrocycles. In the binucleating ligand, I, each fourteen-membered macro



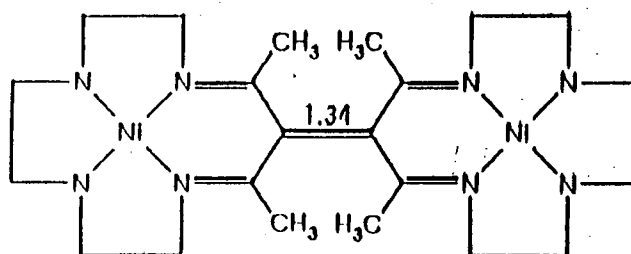
cycle contains β -imine nitrogens with a double bond between corresponding bridgehead carbons. This structure has been established by an X-ray crystallographic determination² of a di-iron (II) complex $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4 \cdot 2\text{CH}_3\text{CN}$, II, which is shown in Figure 1. (CAUTION: Perchlorate salts are known to be explosive.)

The binucleating ligand provides a delocalized π system to promote interaction between the two metal atoms. At the same time, the macrocyclic metal binding sites impart thermodynamic stability and inhibit metal dissociation. By virtue of its structure, the di-iron compound exhibits several unusual properties, among which is an intense absorption band in the near-infrared with $\epsilon = 14,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 874 nm in acetonitrile. (Figure 2) In fact, it was because of this band, which we found during the preparation of a related monomeric macrocyclic compound³, that we became interested in isolating and investigating II.

A schematic representation of the molecule is shown (Figure 3), which gives bond lengths and angles. There is a center of symmetry midway in the bond linking the two macrocycles. The iron atoms and the tetraiminoethylene moiety fusing the two macrocycles are coplanar (average deviation per atom $\pm .02 \text{ \AA}$). The C-C' bond linking the

macrocycles is 1.41 Å, which corresponds to only about 40% double-bond character⁴, indicating conjugation in the tetraiminoethylene moiety. To be consistent with this degree of conjugation, the other C-C bond should have 30% double-bond character and a 1.43 Å bond-length while the C-N bond should have a 70% double-bond character with a bond-length of 1.29 Å, both in quite good agreement with the bond lengths found. (Figure 3)

There is one report in the literature of a crystal structure of a related double-bond bridged dimer⁵, a di-nickel bis 13-member macro-



cycle. An important distinction between the nickel dimer and II is that the methyl groups of the nickel compound interact, causing a displacement of the bridging carbons from the planar array of the nickel and the C, N of the imine bonds. This prevents conjugation in the π electron system and leads to a normal C=C double bond length of 1.34 Å. The nickel dimer has spectral properties similar to monomeric nickel complexes while our di-iron complex has the intense absorption band at low energy mentioned above.

There are three prominent bands at 240, 340, and 874 nm in the unusual electronic spectrum of II in acetonitrile. The high intensities of the bands rule out metal-centered d-d transitions. The transitions are then either ligand-centered or involve some type of charge transfer between metal and ligand. It is well known that complexes containing an

imine bonded to iron (II) exhibit an intense absorption band in the visible region.⁶ This band has been assigned to an Fe to ligand charge transfer (MLCT).⁷ Busch and co-workers in their thorough work on monomeric complexes of iron (II) with unsaturated tetraaza macrocycles observed such MLCT bands with maxima in the 300 to 550 nm range.^{8,9} None of their di, tri, or tetra imine macrocyclic complexes has an intense electronic band anywhere near the low energy band for II. In fact, we are not aware of any iron (II) complex that has a similar spectral feature.¹⁰ Therefore, it seems reasonable to assign the near-infrared band to an MLCT that involves transfer of an electron from filled d_{xz} , d_{yz} orbitals of Fe to a particularly low-lying delocalized π^* orbital of the tetraiminoethylene moiety.

Resonance Raman measurements may prove very helpful in confirming and elucidating the electronic transitions and are planned. Calculations of the energies of the HOMO and LUMO orbitals of II as well as INDO/S¹² calculations of the spectrum are also under way. The energies of the two long wavelength transitions are extremely sensitive to solvent or to the addition of coordinating ligands such as cyanide. It is likely that the axial CH_3CN ligands of II can be replaced; this chemistry is also being explored.

The di-iron compound exhibits other very interesting properties. The dark green $\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}$ complex can be oxidized electrochemically to a yellow species, which can then be reduced quantitatively to the original chromophore. Isosbestic points are observed during the electrochemical oxidation as the 874 nm band of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}$ compound is replaced by a slightly more intense band at 940 nm. The yellow oxidized form is probably an $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ mixed-valence species and we are actively pursuing

its characterization. It appears to have the type of ESR spectrum characteristic of interacting magnetic dipoles¹³ but we have not yet completed the analysis.

Ligand I is the only example to date of a fused, conjugated, bis macrocycle. It is obtained as a di-iron complex.³ However, the structure may prove to be more general. We have spectroscopic evidence that similar di-iron species are generated using 13 and 15 membered macrocycles. Other variations may also be possible. We are especially interested in replacing the iron atoms with other metals, such as copper and nickel, and are working to isolate the free ligand.⁹

Acknowledgment: HSM and LOS wish to thank the Associated Western Universities for student and faculty sabbatical research support respectively. This work was supported, in part, by the Office of Basic Energy Sciences, Chemical Sciences Division of the Department of Energy under Contract No. DE-AC03-76SF00098.

Supplementary Material Available: Table of atomic positional and thermal parameters (1 page). Ordering information is given on any current masthead.

References

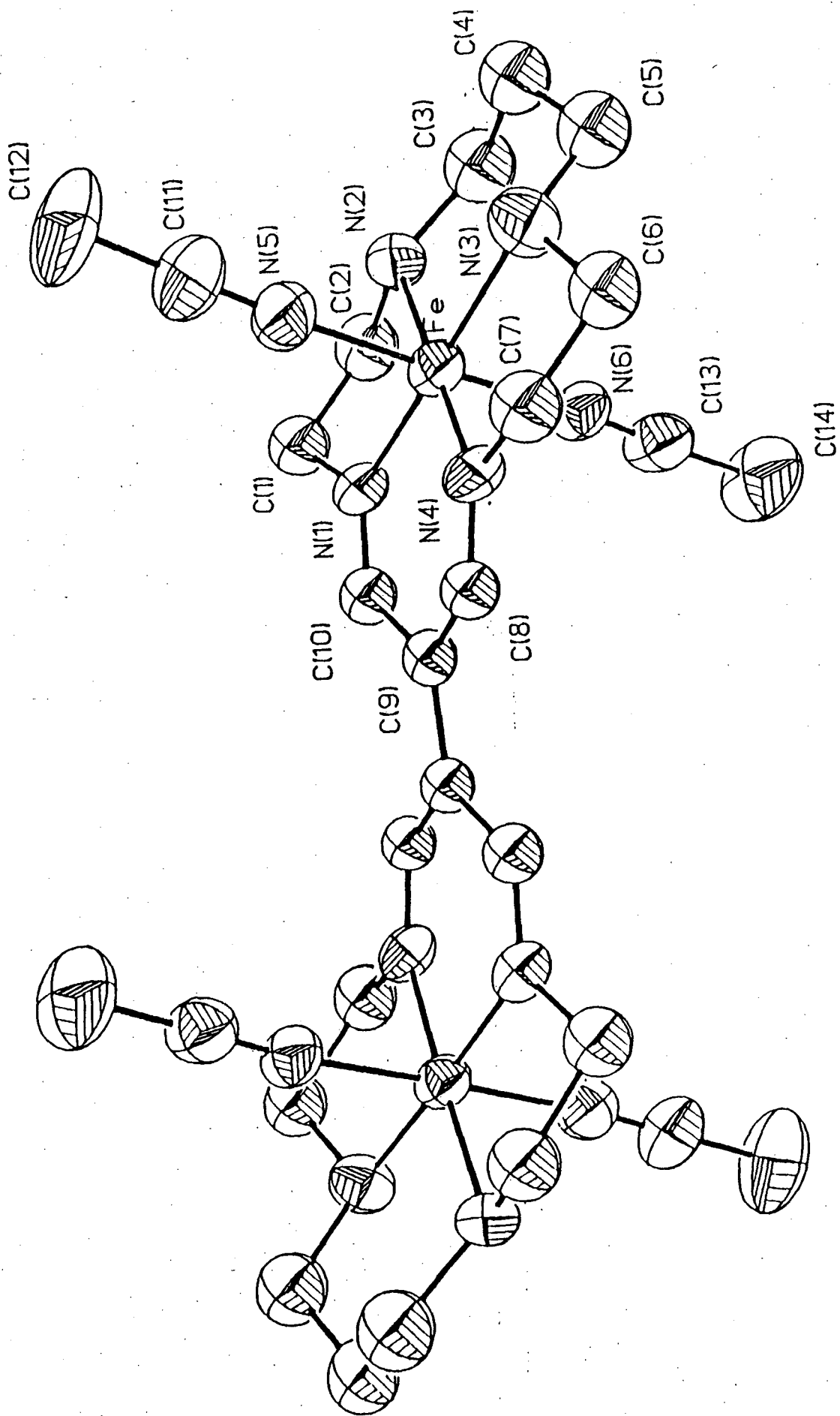
1. a) University of the Pacific
b) Lawrence Berkeley Laboratory
c) Washington State University
2. Crystal class: monoclinic; Space group: $P_{21/n}$; Lattice constants: $a=13.145(8)$, $b=10.909(4)$, $c=17.910(6)$, $\beta=95.53(4)$; $\rho_{\text{calc}}=1.48$, ($Z=2$). For 3747 observed reflections and 257 parameters, the discrepancy indices are $R = .0871$, $R_w = .0866$. (X-ray crystallography questions should be addressed to K.J.B. at Washington State University.)
3. Compound **II** is prepared by combining 1,4,8,11 tetraazacyclotetradecane and $\text{Fe}(\text{OH}_2)_6(\text{ClO}_4)_2$ in oxygenated acetonitrile. The deeply colored purple solution is allowed to stand for several days during which time dark green crystals of **II** form.
4. L. Pauling, *The Nature of the Chemical Bond*, Cornell U. Press, 2nd edition, 1940, 164, 174
5. Cunningham, J. A. and Sievers, R. E., *J. Amer. Chem. Soc.*, 1973, 95, 7183-7185
6. Krumholz, P.; *J. Chem. Soc. A.*, 1953, 75, 2163-2166
7. König, E.; *Coord. Chem. Rev.*, 1968, 3, 471-495
8. Goedken, V. L., and Busch, D. H.; *Inorg. Chem.*, 1972, 11, 7355-7363
9. Riley, D. P., Stone, J. A.; and Busch, D. H.; *J. Amer. Chem. Soc.*, 1976, 98, 1752-1762
10. M. P. Suh, *et al*¹¹, have reported a similar spectrum which was assigned to a monomeric Fe(II) tetraene tetraaza macrocycle. However, the synthetic procedure and other reported properties convince us that they had, in fact, produced **II**.
11. Suh, M. P., Kang, S-G., Woo, K. W.; *Daehan Hwahakhoe chi*, 1984, 28, 384-393
12. Anderson, W. P., Edwards, W. D., and Zerner, M. C.; *Inorg. Chem.*, 1986, 25, 2728-2732
13. Poole, C. P., Jr.; *Electron Spin Resonance*; Interscience, N.Y., 1967 pp 822-825

Figure Captions

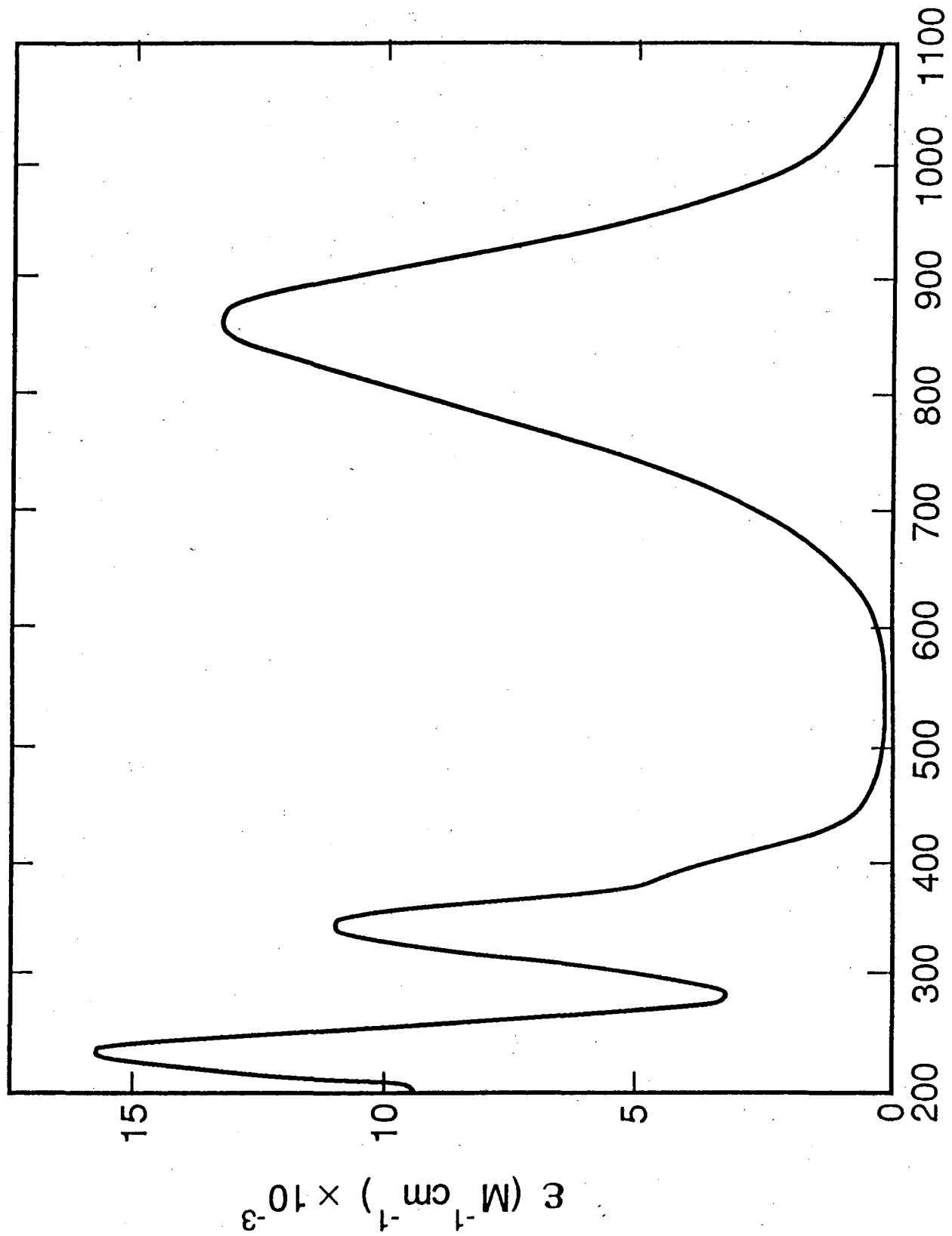
Figure 1. Ortep of $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4]^{4+}$ II. The counter-anions are perchlorates and there are two CH_3CN of crystallization.

Figure 2. Absorption spectrum of II in CH_3CN solution.

Figure 3. Bond lengths and bond angles in complex II. There is a center of inversion midway in the bond linking the macrocycles. Axial CH_3CN molecules are omitted.



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λ (nm)

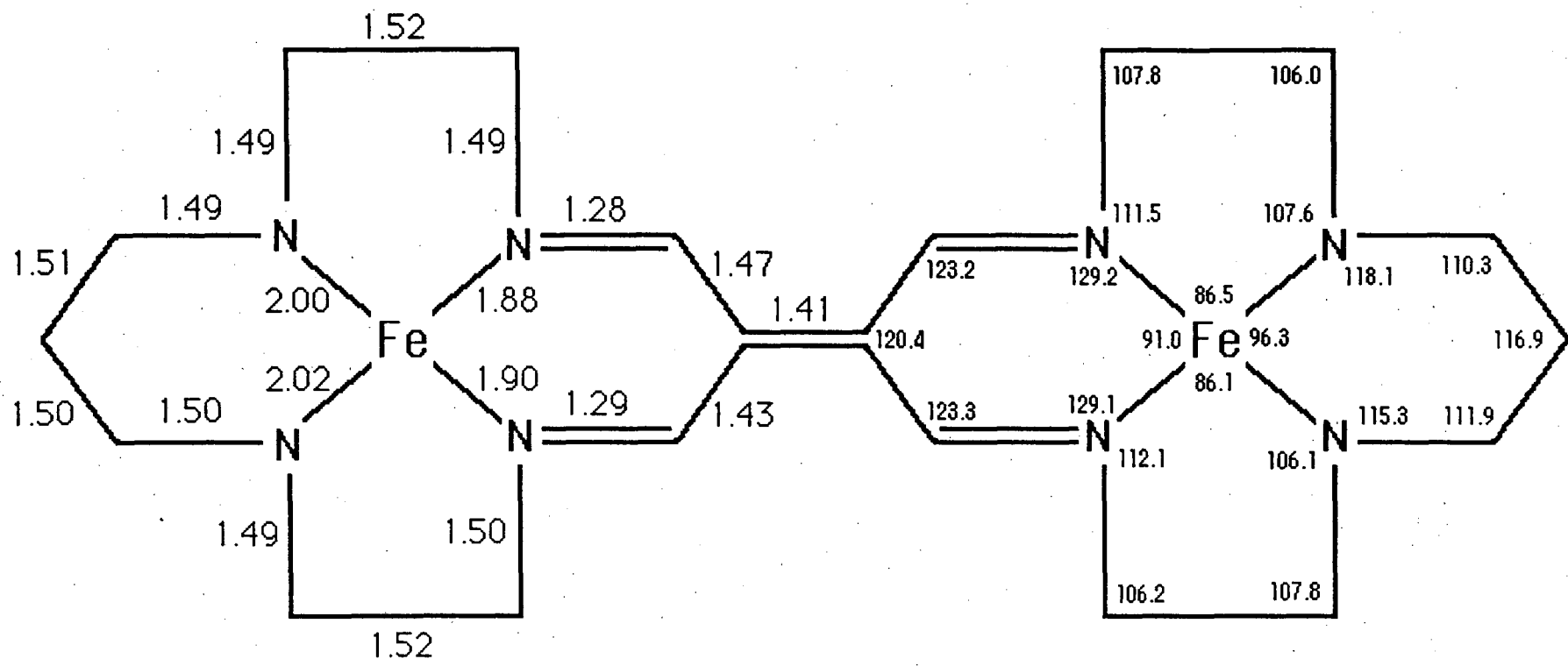


Fig 3

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