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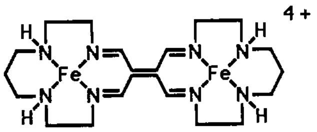
Structure and Properties of a Bimetallic Complex with a Conjugated Bridge between Iron Atoms in Two Macrocycles

We have synthesized and isolated a bimetallic compound that is unique in that it contains a conjugated bridge with extensive delocalization of π electrons between metals in two macrocycles. In the diiron complex



each fourteen-membered macrocycle contains β-imine nitrogens and there is a double bond between corresponding bridgehead carbons. This structure has been established by an X-ray crystallographic determination[1] of the complex $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4 \cdot 2CH_3CN$ (I), which is shown in Figure 1. (*Caution*! Perchlorate salts of transition metal complexes are known to be explosive under conditions of mild shock and heat.)

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 the loss of metal from the complex. By virtue of its structure, the diiron compound exhibits several unusual properties, among which is an intense absorption band in the near infrared with $\epsilon = 14000\ M^{-1}\ cm^{-1}$ 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 compound,[2] that we became interested in isolating and investigating I.

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 tetraimino ethylene moiety fusing the two macrocycles are coplanar (average deviation per atom ±0.02 Å). The C–C′ bond linking the macrocycles is 1.41 Å, which corresponds to only about 40% double-bond character,[3] indicating delocalization in the tetraimino ethylene moiety. To be consistent with this degree of delocalization, 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).

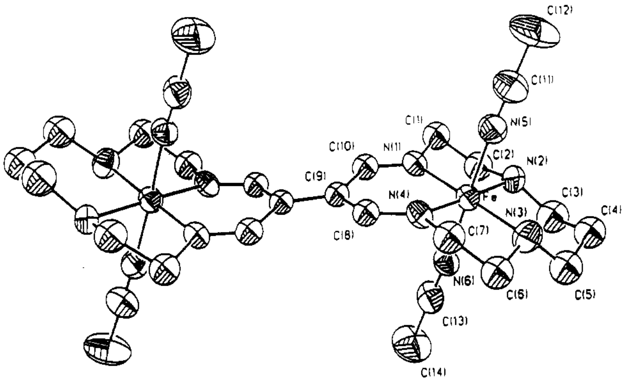


Figure 1. ORTEP of $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4]^{4+}$ (cation of I). The counteranions are perchlorates, and there are two CH_3CN molecules of crystallization.

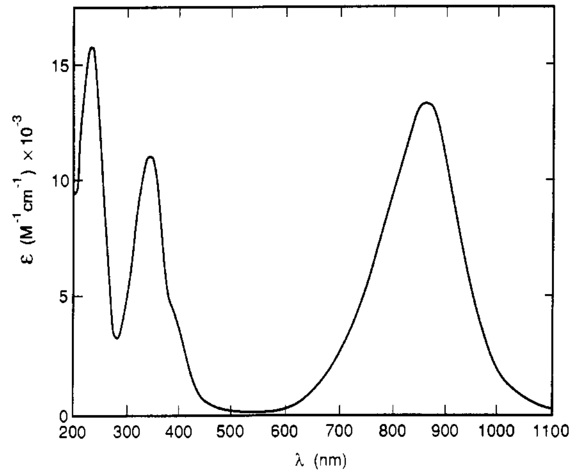


Figure 2. Absorption spectrum of I in CH_3CN solution.

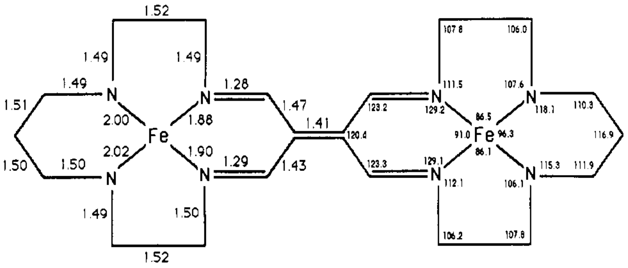


Figure 3. Bond lengths and bond angles in complex I. There is a center of inversion midway in the bond linking the macrocycles. Axial CH_3CN molecules are omitted.

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(1) Crystal class: monoclinic. Space group: $P2_1/n$. Lattice constants: a = 13.145 (8) Å, b = 10.909 (4) Å, c = 17.910 (6) Å, β = 95.53 (4)°. ρ_{calc} = 1.48 (Z = 2). For 3747 observed reflections and 257 parameters, the discrepançy indices are R = 0.0871 and R_w = 0.0866.

(2) Compound I is prepared by combining 1,4,8,11-tetraazacyclotetradecane and $Fe(OH_2)_6(ClO_4)_2$ in oxygenated acetonitrile. The deeply colored purple solution is allowed to stand for several days, during which time dark green crystals of I form.

(3) Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell U. Press: Ithaca, NY, 1940; pp 164, 174.

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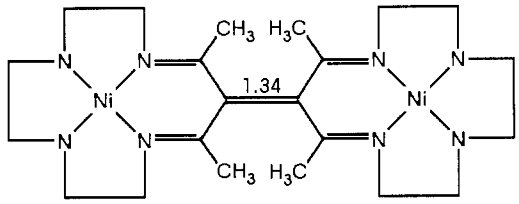
There is one report in the literature of a crystal structure of a related double-bond bridged dimer,[4] a dinickel bis 13-member macrocycle.



An important distinction between the nickel dimer and I 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 C, N of the imine bonds. This displacement effectively prevents delocalization in the π electron system. Thus, the bond between the bridgehead carbons is 1.34 Å, typical of a localized C–C double bond. Also, the imine N, C distances are within the range expected for a localized C=N, and the bond distance between the bridgehead carbon and the carbon of the imine is 1.50 Å, close to a C–C single bond.

Superficially, then, the nickel dimer structure is a precedent for our new compound. However, in the nickel complex the bonding parameters clearly indicate the presence of alternating, isolated double and single bonds due to interactions of the methyl groups. In I, the planar structure promotes extensive delocalization in the π electron system. We believe this delocalization leads directly to the unusual intense low-energy electronic absorption band (see below).

The iron(II)–nitrogen distances of the complex are also unusual. The iron–imine nitrogen distances of 1.88 and 1.90 Å are the shortest that we could find in a search of the Cambridge Crystallographic Data Base. They are about 0.1 Å shorter than the iron(II)–nitrogen distances observed in porphyrin complexes, and the observed iron(II)–nitrogen distances in 1,10-phenanthroline or bipyridine complexes cluster around 1.97 Å.[5] The iron–nitrogen bond distance in a monomeric tetraene 14-membered macrocycle with two α-diimines is 1.954 Å.[6]

The short iron–nitrogen distances may arise from two independent effects. The first is a constriction imposed by the macrocyclic ligand. However, the iron–aliphatic nitrogen bond distances in the current complex fall within the range found for low-spin iron(II) bound to saturated nitrogen donors. Furthermore, the remaining bond lengths and the angles found throughout the saturated portion of the macrocycle are typical for a fourteen-membered macrocyclic complex. These observations indicate there is no particular strain in fitting the relatively small low-spin iron(II) into the macrocyclic cavity.

A more plausible explanation for the short Fe–N distance is that a strong bond is formed due to extensive overlap which develops between metal and nitrogen orbitals when the nitrogen is in the delocalized electron system of the ligand. Another contribution may be back-bonding of iron(II) to antibonding π orbitals of the delocalized imine moiety. As already noted, the observed C=N bond lengths in I are slightly longer than an isolated imine linkage of about 1.27 Å, which is also consistent with extensive delocalization in the ligand.

There are three prominent bands at 240, 340, and 874 nm in the unusual electronic spectrum of I 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.[7] This band has been assigned to an Fe to ligand charge transfer (MLCT).[8] 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 300–550-nm range.[9,10] However, none of their di-, tri-, or tetraimine macrocyclic complexes has an intense electronic band anywhere near the low-energy band for I. In fact, we are not aware of any iron(II) complex that has a similar spectral feature.[11] 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.

Supporting evidence for this assignment comes from the large solvent dependence of the electronic spectrum. Spectra of I in deoxygenated DMF or deoxygenated water also exhibit three prominent bands. The near-infrared band shifts to yet longer wavelengths (λ_{max} 1050 nm in DMF and 1005 nm in water). Also addition of NaSCN to a solution of I in acetonitrile shifts the low-energy band to 1125 nm. We attribute these shifts to ligand exchange with the axial acetonitriles of I. Clearly, the energy of the near-infrared band is very sensitive to the environment around the iron and this is consistent with its assignment as an MLCT.

Further characterization of this interesting new complex is under way.

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Supplementary Material Available: Table SI, listing atomic coordinates for $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4\cdot 2CH_3CN$ (1 page). Ordering information is given on any current masthead page.

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(11) M. P. Suh et al.[12] have reported a similar spectrum, which was assigned to a monomeric iron(II) tetraene tetraaza macrocycle. However, the synthetic procedure and other reported properties convince us that they had, in fact, produced I.

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Is Intramolecular Hydrogen-Bonding Important for Bleomycin Reactivity? A Molecular Mechanics Study

Bleomycins (BLMs) are a class of natural products which are used clinically as antitumor antibiotics and which have been shown in vitro to bind metal ions.[1] It is believed that a species derived