Monocarbon Monoxide Complexes of Iron(II): Synthesis and *X*-Ray Structural Characterization

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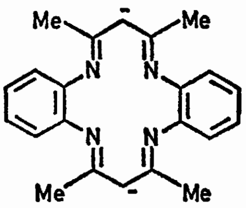
Summary Several monocarbon monoxide complexes of iron(II) with a macrocyclic ligand have been prepared, and a crystal structure of one of these complexes shows that the Fe–C≡O angle is linear, 178°, with an Fe–C distance of 1·75 Å and an unusually long axial Fe–N distance of 2·12 Å.

An understanding of the binding of small molecules such as O_2, CO, NO, and H_2S to iron in biological heme systems is important. The study of synthetic macrocyclic complexes of iron(II) has established the role of many structural parameters of the ligands in influencing iron reactivity.[1] We report on the synthesis and structural characterization of some monocarbon monoxide complexes of iron(II) of the completely conjugated dianionic 14-membered macrocyclic ligand (I). The ligand was first prepared by the template condensation of *o*-phenylenediamine with pentane-2,4-dione on nickel(II) by a modification of Jaeger's method.[2] The ligand was then stripped from nickel(II) with anhydrous HCl in ethanol and isolated as the hydrochloride salt. Neutralization with base afforded the neutral ligand. Monocarbon monoxide complexes of the type $[Fe(C_{22}H_{22}N_4)(base)CO]$, where base = acetonitrile, pyridine, 4-picoline, or hydrazine, were prepared by the reaction of the free ligand with an anhydrous source of iron(II) usually as an amine complex, under an atmosphere of carbon monoxide.[3]† The carbon monoxide stretching frequency for these low spin, diamagnetic complexes was in the range 1930—1940 cm^{-1} which is slightly lower than that observed in native carbon monoxyhemoglobin, 1951 cm^{-1}.[4]



Crystals of the carbon monoxide complex, $[Fe(C_{22}H_{22}N_4)(NH_2NH_2)CO]$, suitable for data collection were monoclinic: space group, $P2_1/c$ with $a = 9{\cdot}422(2)$, $b = 11{\cdot}015(1)$, $c = 21{\cdot}264(4)$ Å, $\beta = 106{\cdot}58(1)°$, $Z = 4$. Intensity measurements from a crystal 0·01 × 0·01 × 0·02 mm mounted nominally about the $10\bar{2}$ axis, were obtained from graphite collimated Mo-K_α radiation on an automated Picker FACS-1 diffractometer. The data were reduced to F's and equivalent reflections were averaged yielding 2802 unique reflections with $F > 2\sigma$. The structure was determined by the heavy-atom technique and refined by conventional least-squares refinement to an $R = 5{\cdot}5\%$.

The Figure shows some of the structural details of the octahedrally co-ordinated low-spin iron(II) complex. The macrocyclic ligand is not flat, but is saddle shaped due to steric interactions of the methyl hydrogen atoms with those of the benzenoid rings. The benzenoid rings are tipped up towards the CO by 18° and 25°, and the six-membered chelate rings are both tipped downwards by 26° relative to the least-squares plane defined by the four nitrogen atoms. The interatomic distances of the ligand indicate a considerable amount of delocalization; most of the C–C distances of the 14-membered inner ring are close to the accepted aromatic C–C distance of 1·397 Å.[5] The average of the four Fe–N distances, 1·94 Å, is significantly shorter than the Fe–N distances found for either low-spin iron(II) or iron(III) porphyrin complexes.[5] This reduction in metal–ligand distance results from the smaller inner ring of the 14-membered macrocyclic ligand compared to the larger core presented by the 16-membered porphyrin rings. The Fe–C≡O angle is essentially linear, 178°, with a short, but normal, Fe–C distance of 1·75 Å. The strong binding of the carbon monoxide molecule by the iron produces a strong *trans* effect resulting in an abnormally long iron–hydrazine bond length of 2·12 Å which is nearly 0·2 Å longer than normally observed for low-spin iron(II)–nitrogen bond distances.[6] The iron is displaced 0·11 Å towards the carbon monoxide from the least-squares plane defined by the four planar nitrogen atoms.

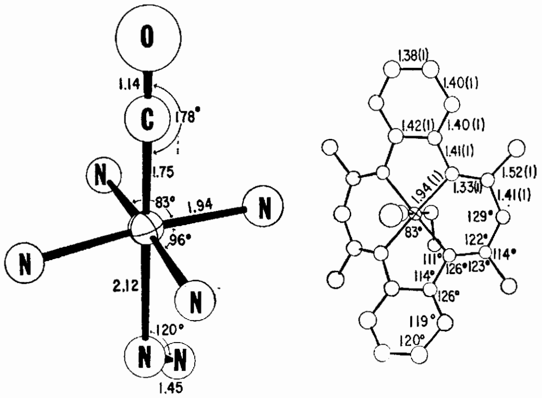


Figure. *Bond distances and angles in the monocarbon monoxide complex,* $[Fe(C_{22}H_{22}N_4)(NH_2NH_2)(CO)]$. *Chemically equivalent distances and angles have been averaged. Numbers in parentheses refer to maximum deviation from average value.*

The formation of these carbon monoxide complexes suggests that co-ordination of monocarbon monoxide to iron(II) is not unique with porphyrin type ligands, but is probably a general phenomenon characteristic of a large

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† All complexes reported give satisfactory elemental analysis.

class of macrocyclic ligands. The results of the *X*-ray structural determination of [Fe($C_{22}H_{22}N_4$)(NH_2NH_2)CO] provide the first detailed structural information of a monocarbon monoxide complex in an environment very similar to that of heme proteins.

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