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LETTER

Bending of the completely conjugated planar macrocyclic iron(II) complex by 1,10-phenanthroline. The crystal structure of $[Fe(II)(C_{18}H_{18}N_6)(C_{12}H_8N_2)](ClO_4)_2$

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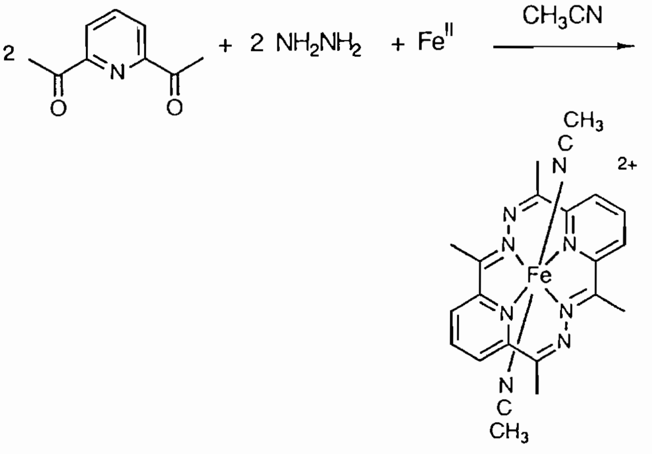
The completely conjugated macrocyclic complexes are of considerable interest due to their rich coordination chemistry and their biomimics of hemes [1–5]. Goedken *et al.* [6] reported the template synthesis and the crystal structure of completely conjugated 14-membered ring hexaaza-ligand complexes, $[Fe(II)L(CH_3CN)_2](ClO_4)_2$.



To account for the large changes of the electronic spectrum when 1,10-phenanthroline was added to the solution of the complex, these authors proposed the folding of the planar macrocyclic ligand. Here we report the crystal structure of the folded complex $[Fe(II)L(phen)](ClO_4)_2$ and compare the structures of the planar and folded complexes.

The complex $[FeL(phen)](ClO_4)_2$ was prepared according to the procedure of Goedken *et al.* [6]. Suitable single crystals were obtained by diffusion of ether into the deep red solution of the complex in acetonitrile. Crystal data of $[Fe(II)L(phen)](ClO_4)_2$:

TABLE 1. Comparison of bond parameters of planar and folded macrocyclic complexes

	Planar complex *trans*-$[FeL(CH_3CN)_2]$	Folded complex *cis*-[FeL(phen)]
Bond lengths (Å)		
Fe–N1[a]	1.892(7)	1.935(4)
Fe–N2[a]	1.899(5)	1.942(3)
Fe–N4[a]	1.938(4)	2.015(4)
N1–N3	1.386(9)	1.398(5)
N1–C2[a]	1.326(9)	1.293(6)
N2–C3	1.344(8)	1.368(6)
N2–C7	1.349(8)	1.368(6)
N3–C8	1.297(9)	1.287(6)
C1–C2	1.518(11)	1.491(7)
C2–C3	1.466(9)	1.451(6)
C3–C4	1.384(11)	1.379(7)
C4–C5	1.391(11)	1.381(7)
C5–C6	1.358(11)	1.361(7)
C6–C7	1.452(10)[b]	1.385(7)
C7–C8	1.476(11)	1.486(7)
C8–C9	1.521(11)	1.500(7)
Selected bond angles (°)		
N1–Fe–N2[a]	83.8(3)	80.41(15)
N1–Fe–N4[a]	88.8(2)	97.14(4)
N1–Fe–N1′[a]	180	150.89(14)
N1–Fe–N2′[a]	96.2(3)	82.08(15)
N1–Fe–N4′[a]	91.2(2)	104.89(14)
N2–Fe–N2′[a]	180	105.47(15)
N2–Fe–N4[a]	90.8(2)	86.74(15)
N2–Fe–N4′[a]	89.2(2)	167.39(15)
N4–Fe–N4′[a]	180	81.28(15)
Fe–N1–N3′[a]	128.4(6)	122.5(3)
Fe–N1–C2	116.3(5)	117.9(3)
N3′–N1–C2	115.3(7)	117.7(3)
N1–C2–C1	125.8(7)	123.7(4)
N1–C2–C3	111.3(7)	113.0(4)
C1–C2–C3	122.9(7)	123.0(4)
N2–C3–C2	115.7(6)	113.0(4)
N2–C3–C4	124.5(7)	121.9(4)
C2–C3–C4[a]	119.5(7)	125.1(4)
C3–C4–C5	121.4(8)	118.6(4)
C4–C5–C6	122.9(9)[b]	119.9(4)
C5–C6–C7	113.4(8)[b]	120.8(4)
Fe–N2–C3	112.7(5)	114.6(3)
Fe–N2–C7	123.6(5)	125.1(3)
C3–N2–C7[a]	123.5(6)	118.8(4)
N2–C7–C6	113.8(7)[b]	119.9(4)
N2–C7–C8	121.1(6)	119.4(4)
C6–C7–C8	124.9(7)[b]	120.5(4)
N3–C8–C7[a]	133.0(7)	126.6(4)
N2–C8–C9[a]	110.5(7)	114.5(4)
C7–C8–C9	116.6(7)	118.9(4)
C8–N3–N1′[a]	117.6(7)	113.6(4)

[a] Significant differences (greater than 3σ). [b] Attributed to the disorder of the planar ligand [6].

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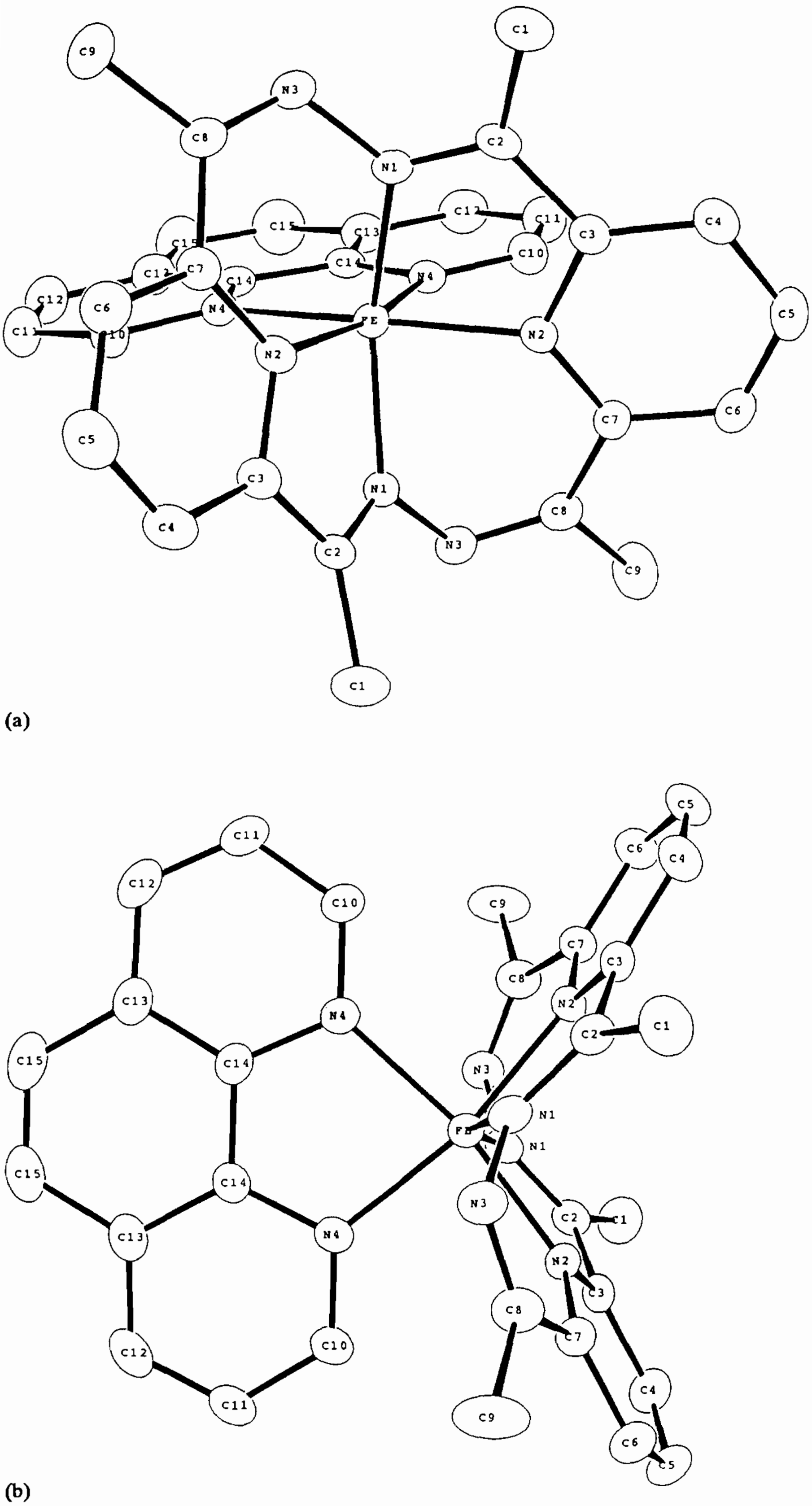

Fig. 1. ORTEP drawing of the cation [FeL(phen)]$^{2+}$ with 50% probability illustrating: (a) the octahedral geometry around the iron(II) ion; (b) the bending of the macrocyclic ligand.

$FeCl_2O_8N_8C_{30}H_{26}$, monoclinic space group $C2/c$, $a = 20.965(3)$, $b = 10.379(2)$, $c = 14.575(7)$ Å, $\beta = 98.24(2)°$, $V = 3139(2)$ Å^3, $Z = 4$, $D_c = 1.564$ g cm^{-3}, $R_F = 0.057$, $R_{wF} = 0.052$ for 2195 unique reflections ($2\theta < 50°$) with $I > 2\sigma(I)$ and 222 variables. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.7093$ Å) radiation. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as fixed contributions. The structure consists of a six-coordinate iron(II) ion girded by four nitrogen atoms of the folded macrocyclic ligand with a 1,10-phenanthroline occupying the *cis* site of the complex (Fig. 1). The complex has crystallographic C_2 symmetry, clearly showing that the original planar macrocyclic ligand is bent into a folded conformation. The folding occurs at the hydrazine nitrogen atoms, confirmed by the large dihedral angle along the hydrazine linkage (dihedral angle of C2–N1–N3′–C8′ is 68.5(5)°). A comparison of bond parameters of these two conformations, the planar and the folded, is presented in Table 1. In the coordination sphere, the folded complex has larger Fe–N distances than the planar one, which are attributed to the crowded coordination sphere of the folded complex. The bond angles around the iron(II) ions of the two complexes differ markedly because of the *cis* and *trans* conformations. In the ligand moiety, the bond lengths of the two complexes are almost identical. There are significant differences in the bond angles around the N1, N3 and C8 atoms. Bond angles are more sensitive than bond lengths when the planar macrocycle is bent along hydrazine single bonds to a folded macrocycle. The structure of the planar complex suffered from a serious disorder. The disorder of the macrocyclic complex cation appeared to be that obtained by rotation of the cation by 180° through the pseudo-twofold axis passing through the nitrogen atoms of the pyridine rings are the iron atom (Fig. 2) [6]. The ratio of the major to minor fraction (disordered) of the cation is 0.7 to 0.3 by refining the nitrogen atoms of hydrazine linkages. Although the structure refinement was carefully done by treating the disordered fraction of the cation as a rigid-body whose geometry was identical with that of the major fraction, but whose orientation was related by a pseudo-twofold rotation axis, the accuracy of the planar structure is limited by this severely disordered macrocyclic ligand.

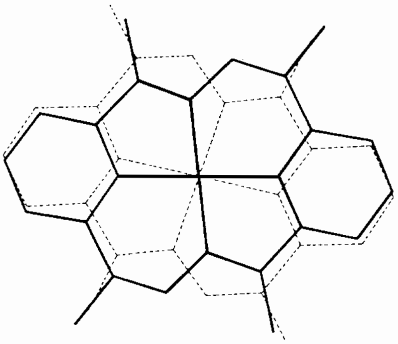

Fig. 2. Diagram illustrating the disorder in the planar cation as viewed down the axial ligands.

Acknowledgement

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