Reactivity of the Four-co-ordinate, S=1, Macrocyclic Complex of Iron(II), [Fe($C_{22}H_{22}N_4$)]: 6,8,15,17-Tetramethyldibenzo[b,i][1,4,8,11]tetra-azatetradeca-2,4,7,9,12,14-hexaenatoiron(II)

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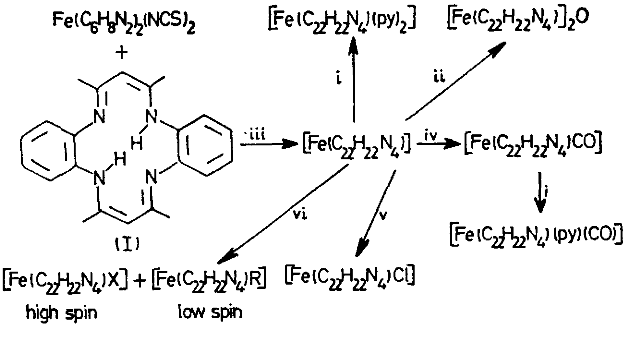
Summary The title four-co-ordinate, S=1, iron(II) complex, [Fe($C_{22}H_{22}N_4$)], has been prepared and reacts with ClO_4^- and alkyl halides to give iron(III) complexes, and with CO to give a five-co-ordinate tetra-aza Fe^{II}–CO complex.

A WIDE variety of macrocyclic ligand complexes have been synthesized and characterized in the past decade.[1,2] The ring size, extent of conjugation, and charge on the ligand profoundly affect the properties of the metal ions, for example, the redox potentials.[3] Despite thorough characterization, the reactivity of these complexes and possible use in catalytic processes has only begun to be explored. We report herein the synthesis and some unusual reactions of a four-co-ordinate Fe^{II} complex.

The reaction of the ligand, $C_{22}H_{24}N_4$, (I) (Scheme) with [Fe($C_6H_8N_2$)$_3$](ClO_4)$_2$, ($C_6H_8N_2$ = *o*-phenylenediamine), in MeCN under N_2 with NEt_3 yields a high-spin, five-co-ordinate Fe^{III} complex, [Fe($C_{22}H_{22}N_4$)Cl], *m/e* 433, $\mu_{eff.}$ 5·95 B.M.† The observation that ClO_4^- was being reduced to Cl^- suggested that a very reactive intermediate, [Fe($C_{22}H_{22}N_4$)] might have been produced. The reaction was then carried out using [Fe($C_6H_8N_2$)$_2$(NCS)$_2$] (Scheme) which



SCHEME. Reagents: i, pyridine; ii, O_2; iii, Et_3N,MeCN; iv, CO, toluene; v, ClO_4^-, $CHCl_3$, or CCl_4; vi, RX.

gave good yields of the four-co-ordinate, S=1, [Fe($C_{22}H_{22}N_4$]: *m/e* 398, $\mu_{eff.}$ 3·69 B.M., vis.-u.v. spectrum: 16,310(sh,

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† All complexes reported gave satisfactory elemental analysis.

ϵ 1795), 17,480(sh, 3029), 18,620(4689), 22,030(4037), 26,320(32,673), 27,930(30,780), and 32,450(26,840) cm^{-1}. It must be pointed out that this four-co-ordinate complex is formed in the presence of the donor ligand, NCS$^-$ and the moderately good donor solvent, MeCN. A few other four-co-ordinate Fe^{II} complexes with S=1 have been characterized, including Fe^{II} phthalocyanines,[4] porphyrins,[5] and another dianionic macrocyclic ligand complex.[2]

The four-co-ordinate [Fe($C_{22}H_{22}N_4$)] complex readily co-ordinates CO in toluene solution giving an unusual five co-ordinate Fe–CO complex, [Fe($C_{22}H_{22}N_4$)CO], ν_{CO} 1921 cm^{-1}. This five-co-ordinate Fe–CO complex readily adds a sixth σ-donor ligand such as pyridine; however, the σ-donor is observed crystallographically to have an abnormally long bond to the iron.[6]

The reactivity towards a number of other reagents is illustrated in the Scheme. The complex is extremely sensitive to O_2, both in solution and in the solid state and forms an oxo-bridged dimer, [Fe($C_{22}H_{22}N_4$)]$_2$O; $\nu_{Fe-O-Fe}$ 890 cm^{-1}, μ_{eff} 1·97 B.M. Of more importance, it reacts immediately with $CHCl_3$ or CCl_4 on mixing, abstracting a Cl atom to form the high-spin, five-co-ordinate complex, [Fe($C_{22}H_{22}N_4$)Cl]. An important extension of this reactivity pattern is the reaction with alkyl halides such as MeI, EtI, or $PhCH_2Br$ to form two types of complexes, a low spin organo-Fe^{III} complex and the five-co-ordinate, S = 5/2, [Fe($C_{22}H_{22}N_4$)X] complexes. The organo-Fe^{III} complexes are identical in all respects to those reported earlier by a different route.[7] It is proposed that the reaction with RX proceeds in a two-step process similar to that determined for $Co(CN)_5{}^{3-}$ in which $Co(CN)_5{}^{3-}$ first abstracts an X atom forming $Co(CN)_5X^{3-}$ and an R radical which then reacts with more substrate forming $Co(CN)_5R^{3-}$ (ref. 8). We have been unable to observe any formation of [Fe($C_{22}H_{22}N_4$)H] with H_2 or other potential sources of H atoms as observed for $Co(CN)_5{}^{3-}$.

A number of factors contribute to the high reactivity of our four-co-ordinate complex. These include: (i) the two negative charges on the ligand greatly stabilize the Fe^{III} state, (ii) the completely conjugated 14-membered ring leads to abnormally short in-plane Fe–N distances and an abnormally high tetragonal ligand field, and (iii) the complex is co-ordinatively unsaturated. The first two aspects mentioned are not as significant for the phthalocyanine and porphyrin ligands. The negative charges on these ligands are delocalized over a much more extensive π-system and the 16-membered inner rings do not appreciably squeeze the metal ion. A reactivity similar to that reported here may be expected for the four-co-ordinate Fe^{II} complex of ref. 2.

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