Nickel(II), Cobalt(II), and Iron(II) Lacunar Complexes having Very Small Cavities: Syntheses, Properties, and Reactions with Dioxygen †

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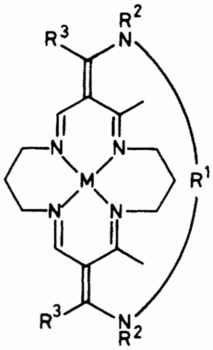
The syntheses and properties of novel lacunar macrobicyclic complexes of a ligand containing a very small cavity around one of the metal-ion axial co-ordination sites are described. The cobalt(II) and iron(II) complexes do not reversibly bind dioxygen under any explored conditions, unlike all other congenors previously reported. This behaviour is presumed to be a consequence of the restrictive volume accessible for dioxygen co-ordination within the cavity of the structure. Despite the lack of dioxygen binding, the iron(II) complex autoxidizes extremely fast, with a second-order rate constant of (7.5 ± 0.5) × 10^{-5} $Torr^{-1}$ s^{-1} at −31 °C; this behaviour constitutes evidence for an outer-sphere electron-transfer oxidation mechanism.

Our previous reports have detailed some of the novel chemistry displayed by the lacunar macrobicyclic complexes of structure (1), Figure 1. In particular, both iron(II) and cobalt(II) complexes of this type have been shown to be unusually effective reversible dioxygen carriers,[1-3] the dioxygen binding constants of which are remarkably sensitive to the nature of the bridge R^1. Figure 1 illustrates the juxtaposition of R^1 with respect to the metal and it is clear that this substituent will dictate the 'head-space' available to any ligand molecule binding within the protected void of the structure. We believe this to be the source of the observed effect of R^1 on K_{O_2}.[1]



(1)

Our work on iron(II) dioxygen carriers of this type had led us to postulate that if R^1 is chosen to be sufficiently sterically demanding, *i.e.* providing a very tight cavity in the structure, then the dioxygen adduct would have a sufficiently small K_{O_2} to allow us to observe reversible O_2 binding without excessive dioxygen activation. Such is indeed the case with the bridge R^1 = $-CH_2C_6H_4CH_2$-*m*- and these complexes have been extensively investigated.[2,3] However, we also sought very small cavities with simple polymethylene bridges in the hope that they may retain some of the reversible O_2 binding behaviour while being less susceptible to oxidation by the bound O_2.‡

A series of such compounds has now been synthesized with R^1 = $(CH_2)_3$, R^2 = R^3 = Me, and M = Ni^{II}, Co^{II}, and Fe^{II}; their properties and reactivities are presented herein. This particular ligand represents that with the smallest bridge length yet prepared and a related major conclusion is of substantial significance. The metal complexes of this ligand appear to remain four- or five-co-ordinate under all circumstances. The indication is that this R^1 bridge is so sterically demanding that a sixth ligand cannot gain access to the axial co-ordination site within the lacuna. This bridged ligand may, therefore, represent a species capable of imposing co-ordinative unsaturation upon a metal ion that would otherwise be octahedral in structure.

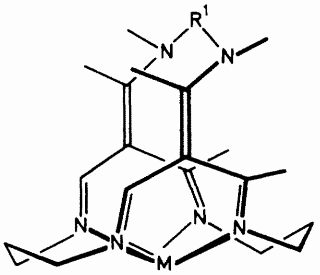


Figure 1. Schematic representation of the lacunar macrobicyclic complexes emphasizing the presence of a rigid cavity around one of the axial co-ordination sites of the metal ion

Experimental

Solvents and reagents were purified as previously described.[4] All syntheses and manipulations of cobalt(II) and iron(II) complexes were carried out under dry, oxygen-free nitrogen in a Vacuum Atmospheres glove-box. I.r. spectra were recorded on a Perkin-Elmer 283B spectrophotometer as Nujol mulls between KBr plates, ^{13}C n.m.r. spectra were obtained in CD_3CN solution with a Bruker WP80 spectrometer at 20.11 MHz and shifts are referenced to $SiMe_4$ (δ = 0). Electrochemical measurements were performed as previously described [4] as were estimates of the dioxygen affinity of the complexes using a Cary 17D u.v.–visible spectrophotometer.[5] E.s.r. spectra were measured on a Varian E-112 spectrometer on both solutions and frozen glasses (−196 °C) with *g* values quoted relative to external diphenylpicrylhydrazyl (*g* = 2.0036). Elemental microanalyses were performed by Galbraith, Inc., Knoxville, Tennessee.

(2,3,7,8,10,16-*Hexamethyl*-3,7,11,15,18,22-*hexa-azabicyclo*-[7.7.7]*tricosa*-1,8,10,15,17,22-*hexaene*-$N^{11}N^{15}N^{18}N^{22}$)*nickel*(II) *Hexafluorophosphate*, $[NiL][PF_6]_2$ [1; M=Ni, R^1 = $(CH_2)_3$, R^2 = R^3 = Me].—[3,11-Bis(1-methoxyethylidene)-2,12-di-

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† *Non-S.I. units employed:* G = 10^{-4} T; Torr = (101 325/760) Pa; B.M. = 9.274 × 10^{-24} J T^{-1}.

‡ The hydrogen atom in the 1-position of the *m*-xylene-bridged materials should be particularly susceptible to radical abstraction by any bound, activated dioxygen species.

methyl-1,5,9,13-tetra-azacyclohexadeca-1,4,9,12-tetraene]-nickel(II) hexafluorophosphate[6] (10 g, 14 mmol) in acetonitrile (250 cm^3) and *NN'*-dimethylpropane-1,3-diamine (1.44 g, 14 mmol) also in acetonitrile (250 cm^3) were simultaneously dripped into 500 cm^3 of refluxing acetonitrile over a period of 2 h. The green solution turned deep orange and removal of solvent gave a brown gum. Chromatography of this gum, in acetonitrile, on Woelm neutral alumina and eluting with acetonitrile, gave a fast moving yellow band which on collection yielded a yellow-orange solid. Recrystallization from acetone–ethanol yielded 1.6 g (15%) of clear orange blocks (Found: C, 36.85; H, 5.20; N, 11.15; Ni, 8.00. Calc. for $C_{23}H_{38}F_{12}N_6NiP_2$: C, 36.95; H, 5.15; N, 11.25; Ni, 7.85%). ^1H N.m.r., δ 7.40 (vinyl H), 3.32, 2.31, and 1.98 p.p.m. (methyl H); ^{13}C n.m.r., δ 171.7, 168.3, 159.2, 113.7, 55.7, 54.9, 50.3, 42.2, 31.3, 29.7, 25.0, 19.7, and 19.5 p.p.m. Molecular weight of neutral material made by deprotonation of the PF_6 salt with NaOMe:[7] 485 [vapour pressure osmometry (v.p.o.) in benzene]; Calc. 454.

The metal-free ligand of this complex, protonated and as its hexafluorophosphate salt, is prepared as previously described for similar lacunar compounds.[7] Exposure of an acetonitrile solution of the nickel complex to anhydrous hydrogen chloride, precipitation from the blue solution of the tetrachlorozincate salt and metathesis in water to the PF_6 salt yields the desired white powdery material. No analytical data were obtained on this material.

$[CoL(NCMe)][PF_6]_2$ [1; $R^1 = (CH_2)_3$, $R^2 = R^3 =$ Me, M = Co(NCMe)].—The ligand PF_6 salt (500 mg, 0.28 mmol) and cobalt(II) acetate tetrahydrate (140 mg, 0.28 mmol) were stirred together in dry methanol (25 cm^3). Sodium acetate (304 mg, 1.12 mmol) was added and the mixture was refluxed for 10 min, whereupon a deep orange solution was present, which on cooling precipitated an orange powder. Evaporating to dryness and extracting into acetonitrile gave a deep orange solution which was reduced to 5 cm^3 in volume before addition of ethanol (15 cm^3) saturated with NH_4PF_6. On standing, orange microcrystals appeared which were collected by filtration and washed with ethanol and diethyl ether to yield 250 mg (65%) of product (Found: C, 38.0; H, 5.15; Co, 7.50; N, 12.35. Calc. for $C_{25}H_{41}CoF_{12}N_7P_2$: C, 38.1; H, 5.25; Co 7.45; N, 12.45%).

$[FeL(Cl)][PF_6]\cdot0.8MeCN$ [1; $R^1 = (CH_2)_3$, $R^2 = R^3 =$ Me, M = FeCl].—The ligand PF_6 salt from above (300 mg, 0.34 mmol) and dichlorobis(pyridine)iron(II) (150 mg, 0.53 mmol) were slurried in acetonitrile (20 cm^3). Addition, dropwise, of triethylamine (0.5 cm^3) caused an immediate colour change from green to deep red. After stirring and refluxing for 10 min the solution was filtered through Celite and methanol (15 cm^3), saturated with NH_4PF_6, was added. On standing, deep violet crystals of the acetonitrile-containing product formed and were collected by filtration, washed with ethanol and ether and suction dried. Yield 204 mg (94%) (Found: C, 44.05; H, 6.20; Fe, 8.25; N, 14.30. Calc. for $C_{23}H_{38}ClF_6FeN_6\cdot0.8CH_3CN$: C, 44.25; H, 6.10; Fe, 8.40; N, 14.25%).

Results and Discussion

Our previous publications[7,8] had expressed some doubt as to whether an R^1 bridge shorter than $(CH_2)_4$ was capable of spanning the parent macrocyclic structure of (1). Efforts at producing a $(CH_2)_3$ bridge by two different routes had failed. Bridging reactions with propane-1,3-diamine aimed at producing [1; $R^1 = (CH_2)_3$, R^2 = H, R^3 = Me] yielded only oligomeric materials,[8] while attempts to produce [1; $R^1 = (CH_2)_3$, $R^2 = R^3$ = Me] using the established general route[7] involving 1,3-ditosylpropane had led to an unusual asymmetric, but still unbridged, structure.[7]

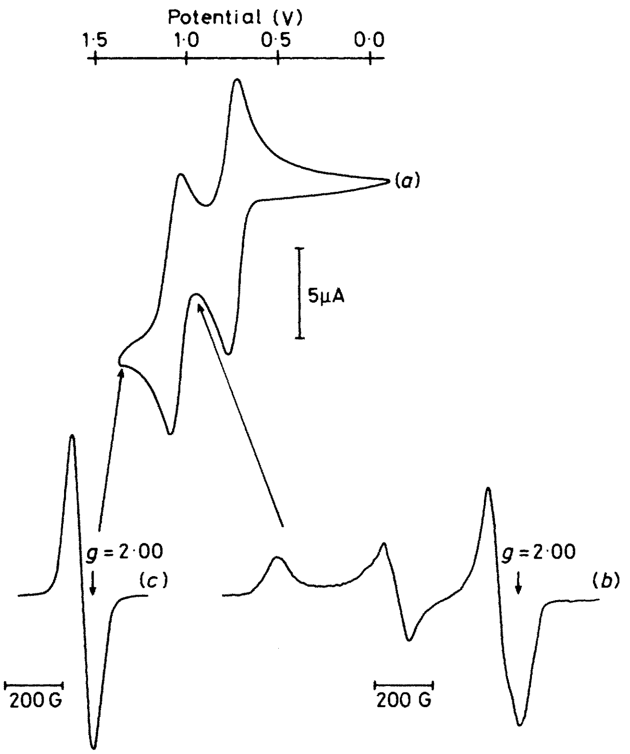

Figure 2. (*a*) Cyclic voltammogram of the complex [1; $R^1 = (CH_2)_3$, $R^2 = R^3$ = Me, M = Ni^{II}]; (*b*) e.s.r. spectrum of a frozen (−196 °C) solution of [1; $R^1 = (CH_2)_3$, $R^2 = R^3$ = Me, M = Ni^{II}] after one-electron bulk electrochemical oxidation at 0.90 V; (*c*) e.s.r. spectrum of a frozen (−196 °C) solution of the same complex after three-electron bulk electrochemical oxidation at 1.3 V

The availability of the diamine *NN'*-dimethylpropane-1,3-diamine suggested a third possible route to this very short bridge length, and using modifications of previously described procedures, the desired compound [1; $R^1 = (CH_2)_3$, $R^2 = R^3$ = Me, M = Ni] was indeed obtained in low yield. The unsuccessful syntheses and the low yield of the successful one indicate that $(CH_2)_3$ corresponds to a bridge length which verges on being too short to span the molecule. Indeed, we have had no success at all in attempts to synthesize the equivalent $(CH_2)_2$-bridged complexes.

The properties of the nickel complex itself are typical of the broader class of lacunar complexes. The i.r. spectrum is clean and sharp with no band assignable to the NH stretching mode. The C=N and C=C stretching vibrations occur at 1 610 and 1 550 cm^{-1} respectively. Both the ^1H and ^{13}C n.m.r. spectra show the expected mirror symmetry of the molecule and v.p.o. measurements in benzene indicate that the molecule is monomeric (see Experimental section).

The electrochemical properties of the complex are interesting because, in addition to the so-called nickel(II/III) redox wave at +0.79 V ($E_{\frac{3}{4}} - E_{\frac{1}{4}}$ = 80 mV), a second highly reversible redox wave appears at +1.11 V ($E_{\frac{3}{4}} - E_{\frac{1}{4}}$ = 60 mV), Figure 2(*a*). Bulk electrochemical oxidation of the yellow solution at 0.90 V shows that the first redox wave corresponds to a one-electron process, but the e.s.r. spectrum of the resultant deep blue frozen (−196 °C) solution, Figure 2(*b*), is not typical of six-co-ordinate nickel(III) species of this class of ligand. Rather, this spectrum reveals the presence of two species, one of which may be a five-co-ordinate nickel(III) complex while the other appears to be an organic radical signal, possibly resulting from ligand oxidation to give $Ni^{II}(L^+)$. At room temperature the e.s.r. solution spectrum displays only this latter 'ligand radical' isotropic signal.

Bulk oxidation at 1.3 V yields even more complex results. While the cyclic voltammogram for the redox wave at 1.11 V is (deceptively) consistent with a reversible one-electron process, Figure 2(*a*), the bulk oxidation does not stop after the passage of two oxidizing equivalents of current. Rather it continues, rapidly to four electrons passed and even thereafter, a small current still flows. Examination of the blue solutions by e.s.r. spectrometry, Figure 2(*c*), shows that as the oxidation proceeds an isotropic signal appears at $g = 2.021$ and grows to maximum intensity as three oxidizing equivalents are passed and then decreases slowly. This isotropic signal does not appear to be the same as that in the one-electron oxidized $Ni^{III}L/Ni^{II}(L^+)$ system [Figure 2(*b*)]. While both signals have the same g value of 2.02, the peak to peak width of that signal is 68 G whereas this signal is only 50 G wide. The behaviour indicates that during the extended time periods associated with bulk electrolysis, the products of the initial two-electron oxidation at 1.3 V can be further oxidized with possible destruction of the oxidized ligand that is produced to give radical products.

The synthesis of the corresponding cobalt(II) complex is straightforward and gives a well characterized, orange microcrystalline product containing one molecule of acetonitrile per cobalt atom that presumably is co-ordinated. The i.r. spectrum of the material is clean and sharp with $\nu(MeC{\equiv}N)$ at 2 288 cm^{-1}, and C=N and C=C stretching bands at 1 622 and 1 543 cm^{-1} respectively. The e.s.r. spectrum of the material in an acetonitrile glass containing 1.5 mol dm^{-3} *N*-methylimidazole (mim) (−196 °C) is typical of this class of low-spin five-co-ordinate cobalt complexes.[1] The axial spectrum has $g_{\parallel} = 2.004$ and $g_{\perp} = 2.294$; $g_{\parallel}$ shows hyperfine coupling to the cobalt nucleus with $A_{\parallel} = 99$ G and superhyperfine coupling to the one co-ordinated nitrogen of the axial mim, $A_N = 13$ G. Exposure of this solution to O_2 (760 Torr) at −50 °C produces no change whatsoever in the spectrum. Even in Me_2CO–mim, exposure to pure dioxygen (760 Torr) at −96 °C produces no e.s.r. spectral change. These results stand in contrast to all other examples of cobalt(II) lacunar complexes where exposure of such solutions to dioxygen at low temperatures leads to production of a dioxygen adduct as evidenced in the e.s.r. spectrum by a typical strong multi-featured absorption centred at $g \sim 2.004$. Also, visible spectra of the cobalt complex in acetonitrile, containing mim (1.5 mol dm^{-3}), show absolutely no spectral change upon exposure to dioxygen (748 Torr) at −41 °C. The conclusion is that this complex has a protected cavity so small as to preclude access by dioxygen on steric grounds, forcing the cobalt centre to remain five-co-ordinate even in the presence of 760 Torr of O_2 pressure at low temperatures.

The electrochemistry of the cobalt complex is fairly typical of this class of compound in that the reversible 'cobalt(II/III)' couple lies at +0.34 V ($E_{\frac{3}{4}} - E_{\frac{1}{4}} = 70$ mV). However, like the corresponding nickel complex, a second highly reversible redox wave occurs at +1.00 V ($E_{\frac{3}{4}} - E_{\frac{1}{4}} = 65$ mV). Bulk electrolysis at 0.65 V gives a green solution whose e.s.r. spectrum is silent as expected for a cobalt(III) species. However, if this solution, sealed from O_2, is allowed to remain at room temperature for extended periods (days) the colour returns to yellow and an e.s.r. spectrum, typical of the cobalt(II) complex, returns. The suggestion is that the five-co-ordinate 'cobalt(III)' species produced during oxidation is unstable with respect to disproportionation to give $Co^{II}L$ and a further oxidized cobalt(III) species. The fact that the returning cobalt(II) signal in the e.s.r. spectrum is approximately 50% of the intensity of that in the original unoxidized sample is consistent with this interpretation. As was the case for the nickel complex, the cyclic voltammogram of the redox wave at 1.00 V seems to correspond well to a reversible one-electron redox process. However, again like the nickel case, bulk electrolysis at 1.2 V does not halt after passage of two electrons per cobalt(II). The current flows steadily up to at least four equivalents during which the e.s.r. spectra of successively more oxidized samples fail to show any significant features. Again we feel that during extended electrolysis, ligand oxidation, and probably cleavage, are responsible for the observations.

The iron(II) complex of this ligand also is readily synthesized using established procedures. The resultant violet crystals contain 0.8 molecules of acetonitrile solvent per molecule of complex, but the anion formulation of chloride–hexafluorophosphate tends to indicate a chloride ion to be co-ordinated as has commonly been observed for other iron(II) complexes of this class.[6,9] The i.r. spectrum of these crystals is very sharp with $\nu(MeC{\equiv}N)$ at 2 246 cm^{-1} and C=N and C=C stretching absorptions at 1 613 and 1 540 cm^{-1} respectively. The complex is high-spin with $\mu_{eff.} = 5.11$ B.M. in acetonitrile solution (Evans n.m.r. method) and is therefore probably five-co-ordinate with a chloride axial ligand. Electrochemistry and conductivity measurements confirm this. Conductivity measurements in dry acetonitrile under N_2 give a molar conductance of 135.4 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} solution. (The acceptable range for a 1 : 1 electrolyte in acetonitrile is 120—160 ohm^{-1} cm^2 mol^{-1}.[10])

The electrochemistry of this complex in acetonitrile has $E_{\frac{1}{2}}$ for the iron(II/III) couple at −0.43 V ($E_{\frac{3}{4}} - E_{\frac{1}{4}} = 60$ mV), which is typical of the five-co-ordinate, chloro–iron(II) complexes of this class. Addition of a strongly co-ordinating axial base, such as pyridine or mim, in ~1 000-fold excess, does not shift $E_{\frac{1}{2}}$. This indicates that the bound chloride is not replaced by such ligands and neither do they enter into the cavity at the sixth co-ordination site. Like the cobalt and nickel complexes, the iron-containing material has a highly reversible ligand oxidation wave at $E_{\frac{1}{2}} = 0.90$ V with $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 70$ mV. It is interesting to note that as the 'metal(II/III)' couple moves more negative in going from nickel to cobalt to iron (0.79, 0.34, −0.43 V) the ligand oxidation shifts in the same direction but to a lesser extent (1.11, 1.00, 0.90 V). This tends to confirm the notion that the ligand oxidation is closely linked to the nature of the metal centre.

Bulk electrolysis of the yellow-red iron(II) complex in acetonitrile at −0.30 V is a one-electron process which gives a deep blue solution whose e.s.r. spectrum is indicative of the formation of high-spin rhombic iron(III) with g values around 6.23, 6.00, and 2.00. Electrolysis at 1.0 V (two equivalents) gives a blue solution whose e.s.r. spectrum appears to retain a large proportion of the high-spin iron(III) signal, but, in addition, contains two new features which appear at $g \sim 2.09$ and 1.97. These presumably represent oxidized ligand radical in the proximity of the paramagnetic metal centre. Again as for the Ni^{II} and Co^{II} complexes, current continues to flow beyond that expected for a simple two-electron oxidation process.

The behaviour of this iron(II) complex with O_2 was unexpected. As stated above, a major reason for synthesizing this ligand was in order to reduce the affinity of the iron complex for O_2 so as to observe reversible O_2 binding. However, results with the cobalt complex suggested that this ligand goes too far in this respect, giving no detectable O_2 binding. It was surprising, therefore, to find that the iron complex in acetone–pyridine–water (3 : 1 : 1 v/v) reacts with dioxygen extremely rapidly, even at −40 °C, leading exclusively to autoxidation products. No spectral evidence could be detected for even transient formation of an O_2 adduct. The reaction proceeds directly from the iron(II) deoxy complex to the iron(III) high-spin product, as judged by electronic and e.s.r. spectra. The autoxidation is clearly first-order in both iron(II) and dioxygen with a second-order rate constant, at -30.9 °C, of $(7.5 \pm 0.5) \times 10^{-5}$ Torr^{-1} s^{-1}. This corresponds to a 12-s half-life for the complex at 760 Torr of dioxygen pressure at -30.9 °C. The full significance of this result will be discussed in a forthcoming publication, but those complete studies support the obvious conclusion that autoxidation proceeds *via* outer-sphere electron transfer from deoxy, five-co-ordinate iron(II) to O_2.

Acknowledgements

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