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Electroactive cryptands containing metallocene units

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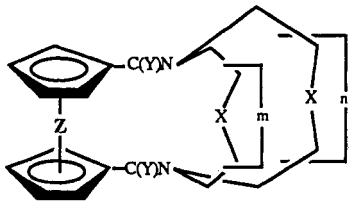
Abstract

Multinuclear nmr and X-ray crystallography are used to determine the structures of cryptands containing metallocene units and their complexes with a variety of metal cations.

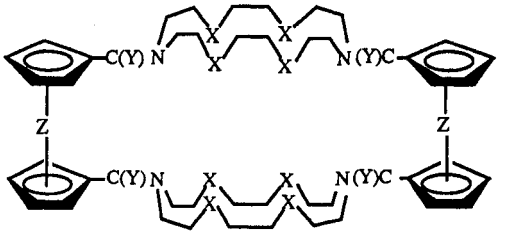
INTRODUCTION

There is currently a great deal of interest in the chemistry of electroactive ionophores[1-4] especially those which may be useful for the detection and/or estimation of specific metal cations by physico-chemical or spectroscopic techniques. In recent years we have studied the synthesis, structure, and



(1)

m,n = 1,2 or 3;
X = O,S,NR;



(2)

Y = O,S,H_2;
Z = Fe, Ru;

cation complexing properties of a range of cryptands (e,g, 1 or 2) containing metallocene units[5,6] and one of the major objectives of this work has been to generate novel, electroactive ionophores. This paper reports recent progress in this area and in particular a study of complex formation between (1, Z=Fe; X,Y=O; m,n=2 or m=2,n=1) and a range of divalent and trivalent cations. A variety of techniques was used including multinuclear nmr, X-ray crystallography and uv/vis spectroscopy. In addition, studies of the reduced form of (2, Z=Fe, X=O, Y=H_2 and m,n=2) reveal the formation of 1: 2, host : guest complexes with a several different cations.

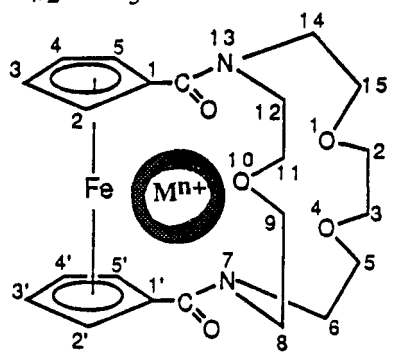
RESULTS AND DISCUSSION

For cryptands of type (1) where Z = Ru, X,Y= O and n,m, = 2 (1a) and when Z = Fe, X,Y = O, m = 2 and n = 1 (1b), X-ray crystallography has shown that the amide carbonyl groups are *trans* to each other[7,4]. Multinuclear nmr shows that the *trans* structure is maintained in solution since (1b) shows a total of twenty two ^{13}C signals comprised of two carbonyl carbons, two ipso carbons, eight ferrocene carbons, six OCH_2 signals and four N-CH_2 signals. Variable temperature ^1H and ^{13}C nmr data show that the energy barrier facing rotation about the amide links is about 17 kcal mol^{-1} corresponding to a half life of about 10^{-2}s at room temprature[8]. Thus on complexation with a variety of

metal cations (e.g. Be^{2+}, Mg^{2+} Ca^{2+}, Sr^{2+} or Ba^{2+}) the amide carbonyl groups rotate into the *cis* configuration forming a bidentate ligand to the cations. This is evidenced by the observation of eleven signals in the ^{13}C nmr of the complexes of (1b) consistent with a plane of symmetry imposed by the *cis* orientation of the carbonyl functions[6]. The complexation could, in principle, occur on the short or long side of the macrocyclic ring and although no X-ray data are available, a combination of ^{1}H COSY and ^{1}H / ^{13}C correlation spectra indicate short-side complexation[6].

An analogous type of complex formation occurs between (1b) and the Y^{3+} cation but the observed stoichiometry is both 2:1 and 1:1 (ligand : Y^{3+}). The ^{1}H and ^{1}C nmr spectra are very similar for both complexes (Table 1) and the tight binding of the carbonyl oxygens to the Y^{3+} cation is illustrated by a

Table 1 ^{1}H and ^{13}C nmr data on the complexes of (1b, Z=Fe; X,Y=O; m=2,n=1) with $Y(ClO_4)_3$ and $Ca(ClO_4)_2$ in CD_3CN



(1b) : M^{n+}

^{13}C data

C atom in (1b) / M^{n+}	(1b) : Ca^{2+} (ppm)	2(1b) : Y^{3+} (ppm)	(1b) : Y^{3+} (ppm)
8/12	50.1	50.1	49.6
6/14	54.2	53.9	53.7
5/15	69.1	68.9	70.6
2/3	71.1	70.9	71.9
9/11	72.9	73.2	73.7
1/1'	77.6	77.2	78.9
2/2'	71.1	70.8	70.8
3/3'	73.7	73.3	72.9
4/4'	73.1	72.9	72.2
5/5'	77.7	77.6	77.5
C=O	173.1(d)*	172.5(d)*	173.1

* $^{2}J_Y$ = 3.0 (+/- 0.2)Hz

^{1}H data : cpd protons

cpd ^{1}H	(1b) : Y^{3+}	(1b) : Ca^{2+}
H2 / 2'	5.18	5.08
H3 / 3'	4.61	4.55
H4 / 4'	4.58	4.57
H5 / 5'	5.09	5.10

coupling constant (^2J_Y) of *ca.* 3Hz for both complexes. The ^{89}Y nmr of the mixture at 12.2 MHz (Bo = 5.9 T) shows an upfield shift -6.7ppm relative to the uncomplexed $Y(ClO_4)_3.4.7\ H_2O$. This signal accounts for 67% of the total yttrium in the mixture and is comprised of an equimolar mixture of the 1:1 and 2:1 (host : guest) complexes. The remaining yttrium appears as a signal at +11.5ppm corresponding to $Y(ClO_4)_3\ 7.6\ H_2O$* which must have been formed by a combination of $Y(ClO_4)_3.4.7\ H_2O$ and water displaced from the latter by the cryptand. The coincidence of the two ^{89}Y signals of the cryptands at -6.7ppm may be explained if it is assumed that the formation of the 1:1 complex involves the displacement of two moles of H_2O by amide groups whereas the formation of the 2:1 complex merely involves extra coordination at the yttrium or possibly replacement of acetonitrile molecules from the solvent sheath with little, if any, change in the ^{89}Y nmr shift.

Unfortunately, no X-ray crystallographic data are available on cation complexes of (1b) to confirm the conclusions from the nmr studies. A crystalline complex between (1c, Z = Fe; X,Y = O; m, n =2) and $Y(ClO_4)_3$ has, however, been isolated. The stoichiometry of the crystalline material proved to be 2:1 (host : guest) and the X-ray crystallographic study≠ revealed a seven coordinate yttrium cation at the centre of a capped trigonal biprism (Fig.1) with the seventh coordination site (the cap) being occupied by a mole of H_2O. Most significantly however, both the host cryptand molecules had their pairs of carbonyl functions in *cis*-configurations to form two sets of bidentate ligands to the yttrium cation thus confirming the conclusions from the nmr data.

Reduction of (2a, Z = Fe; X,Y = O; m, n = 2) by $LiAlH_4$ in CH_2CH_2/THF[10] led to (2b) with Y = H_2. The ^1H and ^{13}C nmr spectra of this molecule were relatively simple with the ^1H nmr showing three sets of protons at 2.7ppm (Fe-CH_2-N), 3.6ppm (NCH_2 + OCH_2) and 4.1ppm (ferrocene hydrogens).Complexation with monovalent (e.g. Na^+), divalent (e.g. Ca^{2+}) or trivalent (e.g. Y^{3+}) cations occured at a stoichiometry of 1 : 2 (2b : cation) and caused downfield shifts of the Fe-CH_2-N, ferrocene hydrogens and ring NCH_2 hydrogens of the host (Fig.2). The OCH_2 hydrogens however, were unaffected and the only ^{13}C signals to register significant shifts were those of the cyclopentadiene ring attached to the CH_2 group (Table 2). One must conclude that the cations within these molecules are bound in close proximity to the iron atoms, possibly by the tertiary amine ligands. Work is in progress to confirm this hypothesis.

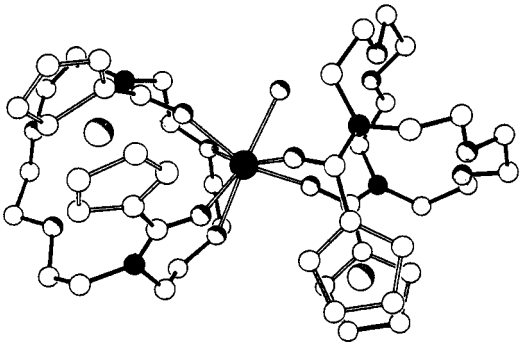


Fig. 1 X-ray crystal structure of the complex between (1c) and $Y(ClO_4)_3$ of molecular stoichiometry 2(1c) : $Y(ClO_4)_3$: $1H_2O$.

Table 2 ^1H and ^{13}C nmr data on the complexes of (2b, Z=Fe; X=O; Y=H_2; m,n=2) with M^{n+}(molar ratio 1 : 2) in $CDCl_3/CD_3CN$

M^{n+}	^{13}C(ppm) Ipso-C	Δδ (ppm)	^1H(ppm) $FcCH_2N$	Δδ (ppm)
None	83.0	-	3.58	-
Na^+	83.0	0	3.82	0.24
Ca^{2+}	79.9	-3.1	3.93	0.45
Y^{3+}	74.4	-8.6	4.55	0.97

* Independent studies have shown that addition of each mole of water to the hydration sphere of Y^{3+} causes a downfield shift in the ^{89}Y spectrum of *ca.* 4ppm.

≠ Data acquired and structure solved by D.J.Williams, Imperial College of Science and technology, London, SW7 2AY.

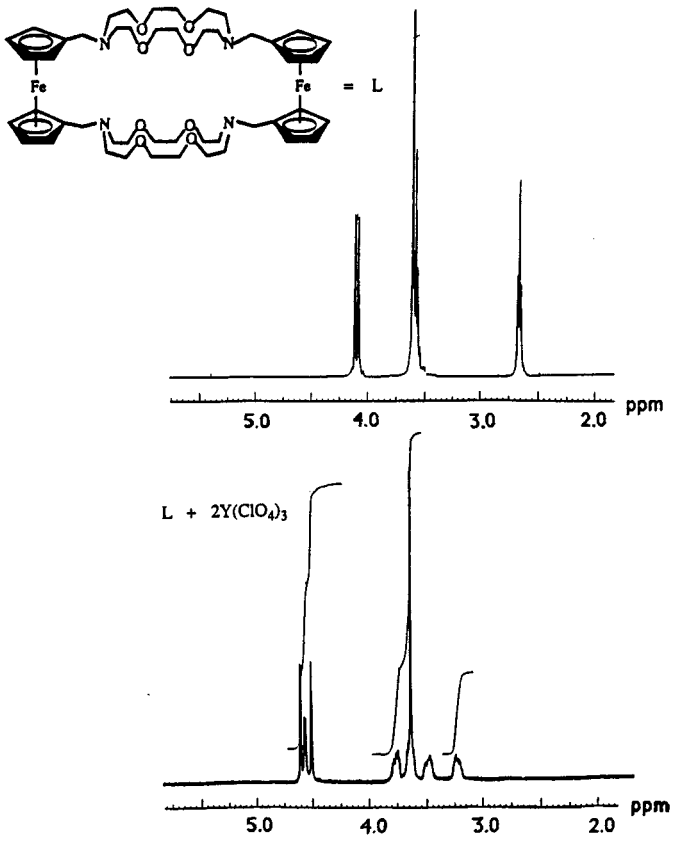


Fig. 2 ^{1}H nmr spectra of (2b) and its complex with $Y(ClO_4)_3$ in CD_3CN

EXPERIMENTAL

The ^{1}H and ^{13}C nmr spectra were recorded in 5mm tubes on a Bruker AM360 MHz instrument operating at 90.6 MHz for ^{13}C spectra. The ^{89}Y nmr data were obtained on a Bruker WM250 operating at 12.2 MHz and using 10mm o.d. nmr tubes. No decoupling was used, relaxation delays were typically 16s and the number of scans was approximately 3000. The complexes between the cryptands and the cations were usually prepared in CH_3CN/CD_3CN as solvent at concentrations in the region of $5x10^{-2}$ - $1x10^{-1}$ M. The ^{89}Y nmr data, however, required the use of higher (0.5M) concentrations.

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