= not measurable, 1 P^3, 1 P^4, 1 P^5], 2.5 (broad signal, 1P^6); ^{195}Pt, δ = −3305 [dd, $^1J(Pt^1P^1)$ = 4105, $^1J(Pt^1P^6)$ = 3242, $^1J(Pt^1Pt^2)$ = 2150, 1 Pt^1], −2893 (broad signal, 1 Pt^2), −2920 [t, $^1J(Pt^3P^4)$ = $^1J(Pt^3P^5)$ = 2872, 1 Pt^3]. If the solution is warmed up and the excess gas is allowed to escape, the starting material, $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$, is obtained. This was confirmed by the ^{31}P spectrum.

Reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with H_2S. H_2S gas was bubbled through a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (10 mL) for 1 min. The product was identified as $[Pt_3H(\mu_3\text{-S})(\mu\text{-dppm})_3][PF_6]$ by its NMR spectra.

X-ray Analysis of $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCOEt})(CO)(\mu\text{-dppm})_3][PF_6]_2$ [7b$(PF_6)_2$]. The specimen was a transparent plate of dimensions 0.36 × 0.48 × 0.08 mm mounted in air. All crystallographic measurements were made on an Enraf-Nonius CAD4F diffractometer using Mo X-rays and a graphite monochromator. The dimensions of the reduced triclinic cell (Table III) are based on a least-squares fit to the setting angles of 22 reflections with $12 \leq \theta \leq 16°$. The intensities of 19 892 reflections with $15 \leq h \leq 15$, $15 \leq k \leq 15$, $25 \leq l \leq 25$, and $\theta < 24°$ were measured from $\omega/2\theta$ scans and corrected for Lp effects and absorption.[21] Merging equivalent intensities gave values for 14 362 unique reflections and R_{int} = 0.030. The analysis was carried out by using the 9028 unique intensities with $I > 2\sigma(I)$. During data collection, the intensities of two standard reflections showed only random fluctuations of ±3% about their mean values.

The structure was solved successfully in the space group $P\bar{1}$ by Patterson and Fourier methods and refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. In the final calculations, fixed contributions were added to the structure factors to account for the scattering of all 72 hydrogen atoms: they were assigned an isotropic displacement parameter 20% greater than that of the parent carbon atom and their positions were deduced geometrically, assuming C–H = 0.96 Å. For Pt, P, and F atoms, anisotropic displacement parameters were refined, whereas isotropic displacement parameters were adjusted for O and C atoms. The 12 phenyl rings were refined as planar rigid groups with C–C = 1.38 Å and ∠C–C–C = 120°. Because of program limitations, the parameters of the cation and those of the two anions were refined in alternate full-matrix least-squares cycles. In the later stages of refinement, five regions of electron density attributed to occluded solvent were observed; distinct molecules of the solvent, which is probably acetone, could not be identified crystallographically, and the five sites were therefore included as carbon atoms in the model, thereby reducing R and R_w from 0.045 and 0.054 to the final values of 0.043 and 0.049. The entries in Table III make no allowance for the unidentified solvent. Parameter shifts were <0.040 of the corresponding esd in the final refinement cycle. Function values in the final difference synthesis were between −1.3 and +1.6 e Å^{-3}. Mean $w\Delta^2$ showed no consistent variation with $|F_o|$ but increased at low $(\sin \theta)/\lambda$. Fractional coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms are presented in Table IV.

Neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 22. Calculations were performed on a Gould 3227 32-bit minicomputer using the locally developed GX program package.[23]

Acknowledgment. We thank the NSERC (Canada) for financial support (to R.J.P.), NATO for a travel grant, Shiraz University for granting leave to M.R., and Mr. C. Anderson for experimental assistance and Dr. J. D. Scott for the DSC experiment.

Supplementary Material Available: Listings of atomic coordinates and isotropic displacement parameters for hydrogen atoms (Table SV), anisotropic displacement parameters (Table SVI), and bond lengths and angles (Table SVII) (6 pages); a listing of observed and calculated structure factors (Table SVIII) (29 pages). Ordering information is given on any current masthead page.

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[21] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

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Complexation of Metal Cations by the Cryptand 1,1′-(1,4,10-Trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene

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Multinuclear NMR spectroscopy has been employed to study the configuration adopted in solution by the 3-fold nonsymmetrically bridged ferrocene-containing cryptand 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene when complexed with the range of metal cations Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. The results show unambiguously that formation of complexes of 1:1 stoichiometry involves coordination of the cations with a cis configuration of the amide carbonyl groups. This results in the creation of a plane of symmetry in the complex, which is not present in the host. The guest cations are selectively coordinated on the short side of the host macrocycle.

Introduction

Cryptands are known to complex metal cations, often selectively.[1] Incorporation of a metallocene unit within the molecular framework of the cryptand yields ionophores capable of forming host–guest complexes within which metal–metal interaction is possible. Thus, ferrocene-containing cryptates have been shown to have useful electrochemical and chromogenic properties[2,3] and hence have potential as molecular sensors.[4] The ferrocene-containing cryptand 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene (1) is 3-fold

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[1] Lehn, J. M. *Pure Appl. Chem.* **1978**, *50*, 871.

[2] Hall, C. D.; Sharpe, N. W.; Danks, I. P.; Sang, Y. P. *J. Chem. Soc., Chem. Commun.* **1989**, 419.

[3] Hall, C. D.; Danks, I. P.; Sharpe, N. W. *J. Organomet. Chem.* **1990**, *390*, 227.

[4] Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409.

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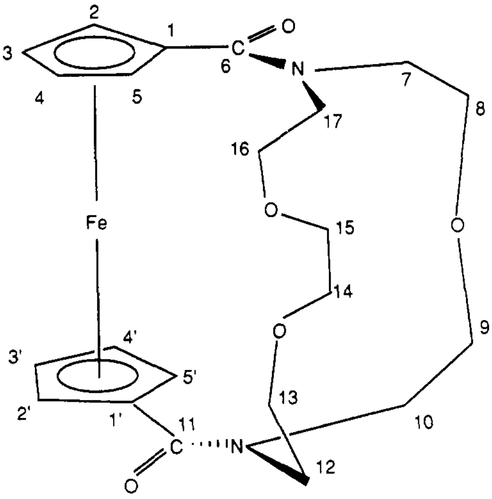

Figure 1. Schematic stereochemical representation of 1 with atom-numbering scheme.

nonsymmetric in its bridging units and as a host therefore offers a variety of potentially selective coordination modes. This study investigates the structural factors of molecular design that influence and determine complexation behavior. The structure of 1 (see Figure 1) is best described as a cryptand in which the apical N atoms are bridged by one short and by one long heterocyclic chain and by a ferrocene unit bonded via amide groups. Crystallographic studies have revealed the structure of 1 in the solid state, and this has been correlated to the structure present in solution by detailed NMR analysis.[5] Equilibrium studies have shown that, for this type of cryptand, the carbonyl functions are essential for strong complexation of alkaline-earth-metal cations but that the O atoms within the heterocyclic bridges are not. However, the heterocyclic bridges do play a role in determining host–guest complexation stoichiometries.[3] For the complexes of 1 with metal cations, only 1:1 host–guest stoichiometries are observed in dilute equimolar solutions. The complexes are difficult to crystallize and are often hygroscopic, and no crystallographic studies have, as yet, been made. Therefore, NMR data for solutions of the complexes 1:M^{2+} have been used to deduce their stereochemical configuration and the results of this study are reported below.

Experimental Section

Synthesis of 1. Solutions of 1,1′-bis(chlorocarbonyl)ferrocene (0.50 g) in toluene (90 mL) and of triethylamine (0.40 mL) mixed with 1,4,10-trioxa-7,13-diazacyclopentadecane (0.35 g) in toluene (90 mL) were added dropwise, separately and simultaneously during 2 h, to vigorously stirred toluene (150 mL, 70 °C) under nitrogen. The mixture was stirred at 70 °C for a further 3 h and then allowed to cool, and the solid material was removed by filtration. The filtrate was evaporated to dryness under reduced pressure to yield a burgundy colored semisolid, which was chromatographed on neutral alumina with dichloromethane (98%)–methanol (2%) as eluent. The orange band was collected, evaporated to dryness under reduced pressure, and triturated with diethyl ether. The product was recrystallized from dichloromethane to yield deep orange crystals of 1, 0.21 g (29%). FAB-MS: *m/z* 457 (1H$^+$). Anal. Found: C, 57.73; H, 6.11; N, 6.07. Calcd for $C_{22}H_{28}N_2O_5Fe$: C, 57.91; H, 6.18; N, 6.14.

Preparation of 1:M^{2+}. The metal cation perchlorates were dried at 120 °C (0.01 mmHg, 3 H). Equimolar solutions of metal perchlorate and 1 in MeCN-d_3 were prepared directly under nitrogen at the required concentration (ca. 5 × 10^{-2} M) by mixing solutions of the cation M^{2+} and of 1. Complex formation is effectively instantaneous and visible to the eye with solutions becoming more red and more intense; 1 has λ_{max} = 451 nm (ϵ = 240 mol^{-1} dm^3 cm^{-1}), while the complexes with the beryllium group cations, 1:M^{2+}, have λ_{max} = 468 (±2) nm (ϵ in the range 320 (±60) mol^{-1} dm^3 cm^{-1}).

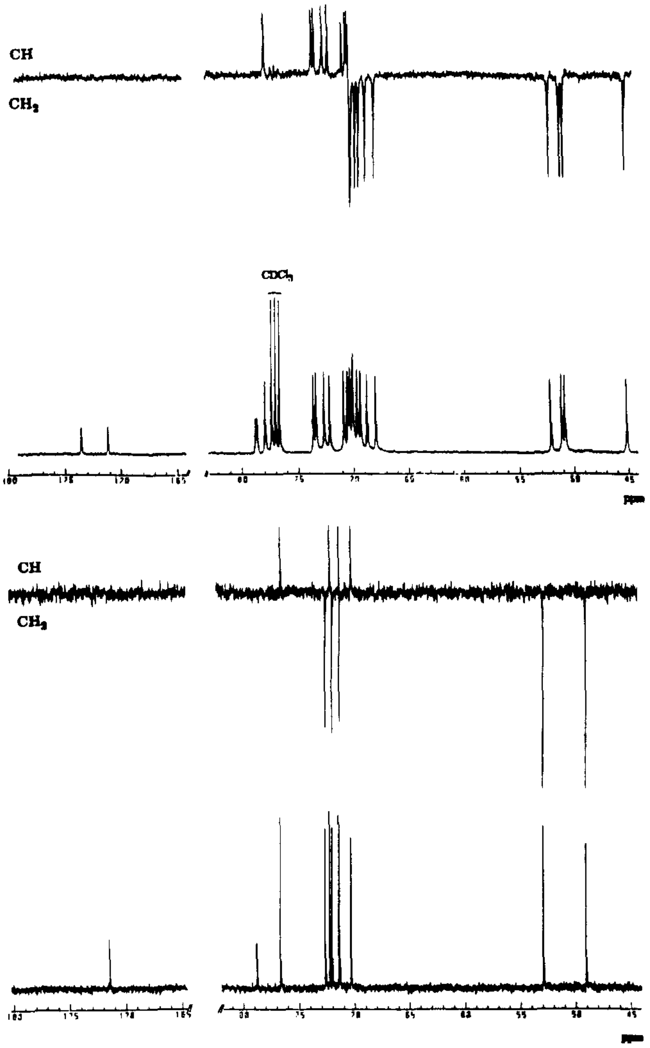

Figure 2. (A) Top: ^{13}C NMR spectrum of 1 in CDCl$_3$ at 5 × 10^{-2} M and 295 K. (B) Bottom: ^{13}C NMR spectrum of 1:Ba^{2+} in MeCN-d_3 at 5 × 10^{-2} M and 295 K. (Note: The ^{13}C spectrum of 1 in CDCl$_3$ is shown for the sake of clarity, since it is almost identical with that in CD$_3$CN. Unfortunately, in CD$_3$CN two pairs of the cluster of 13 resonances in the region 68–75 ppm overlap.)

NMR data were recorded on a Bruker AM 360-MHz instrument by using the CD$_3$CN lines at 1.93 ppm for ^{1}H and at 1.30 ppm for ^{13}C as reference signals.

Results and Discussion

NMR Analysis. The ^{13}C chemical shift data for 1 in MeCN-d_3 solution are listed in Table I and assigned to the solution structure shown in Figure 1, which includes the atom-numbering scheme. The spectrum is almost identical with that reported for 1 in CDCl$_3$ solution for which signals have been assigned unambiguously in relation to the known crystal structure.[5] The molecule, as illustrated in Figure 1 with the carbonyl groups trans to each other, has no element of symmetry, and therefore each ^{13}C nucleus gives rise to an unique resonance in the ^{13}C NMR spectrum (Figure 2A).

For an equimolar solution of 1 with barium perchlorate, pronounced changes in the ^{13}C and ^{1}H NMR spectra are observed. The ^{13}C NMR spectrum of the complex 1:Ba^{2+} is shown in Figure 2B. The most obvious change is a

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[5] Hall, C. D.; Danks, I. P.; Nyburg, S. C.; Parkins, A. W.; Sharpe, N. W. *Organometallics* **1990**, *9*, 1602.

Table I. ^{13}C Chemical Shift Data (ppm) for the Ferrocene-Containing Cryptand 1 in CD_3CN at ca. 5×10^{-2} M and 295 K

atom	$\delta(^{13}C)$	atom	$\delta(^{13}C)$
C7	45.94	C3′	71.01
C10	50.76	C4	71.01
C12	51.64	C3	71.52
C17	52.91	C4′	72.81
C9	69.09	C5	73.78
C14/C15	69.90	C2′	73.78
C13	70.12	C2	74.16
C16	70.48	C5′	78.49
C8	71.08	C1/C1′	80.37
C14/C15	71.26	C1′/C1	80.58
		2 × C=O	171.13
			173.71

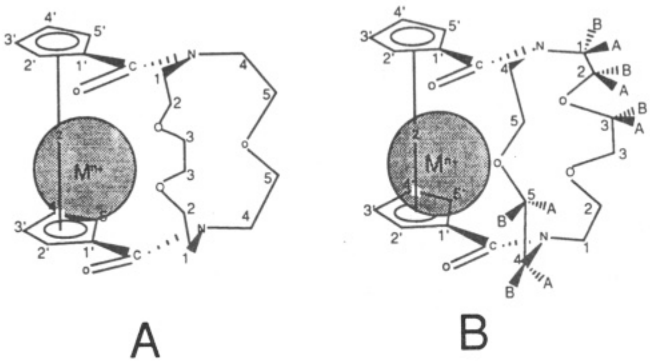

Figure 3. Stereochemical representations of the complex 1:M^{2+}: (A) with coordinating carbonyl groups cis to the long heterocyclic bridge and (B) with coordinating carbonyl groups cis to the short heterocyclic bridge. In (B) atoms A and B are hydrogens.

reduction in the number of signals observed in both the ^{13}C and ^1H spectra to precisely half their original number. For example, in the region 45–55 ppm where the NCH_2 nuclei are observed clearly as the resonating species, four signals in the ^{13}C spectrum of 1 are observed, whereas two signals are observed in the ^{13}C spectrum of 1:Ba^{2+} (Figure 2). Also, the two $^{13}C{=}O$ signals in 1 become one signal in the complex, the Fe*C* signals (distinguished by DEPT) become five from ten, and the OCH_2 signals reduce in number from six to three. Therefore, the complex 1:Ba^{2+} must possess an element of symmetry. Figure 3 shows two proposed solution structures for the complex, both of which contain a plane of symmetry. No other structures of 1:1 host–guest stoichiometry are possible in which the number of magnetic environments within the uncomplexed host macrocycle reduce upon complexation by a factor of 2. Therefore, the NMR spectra of 1:Ba^{2+} prove conclusively that the carbonyl groups must be cis in order to accommodate complexation of the cation. Also, in 1:Ba^{2+} the cyclopentadienyl (Cp) rings become eclipsed, as do the amide groups, with the plane of symmetry bisecting the whole complex in a plane midway between the Cp rings. By contrast, in the uncomplexed host 1 the carbonyls are trans and the Cp rings are not eclipsed with the amide substitution at the Cp rings staggered (by 71.7° in the solid state).[5] Variable-temperature studies on 1 have shown that the free energy of activation for amide rotation, $\Delta G^{\ddagger}$, is 63 kJ mol^{-1} at room temperature,[6] which corresponds to a half-life for amide rotation at ambient temperature of ca. 0.01 s. Although this is slow on the NMR time scale, it is fast enough to allow the cis configuration of carbonyl groups within the host to be formed, which is necessary to complex the cation.

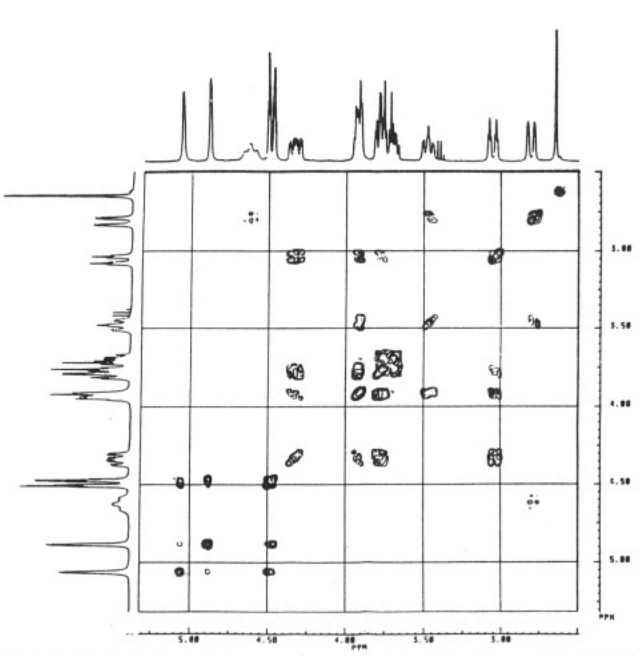

Figure 4. 2-D COSY spectrum of 1:Ba^{2+} in MeCN-d_3 at 5×10^{-2} M and 295 K.

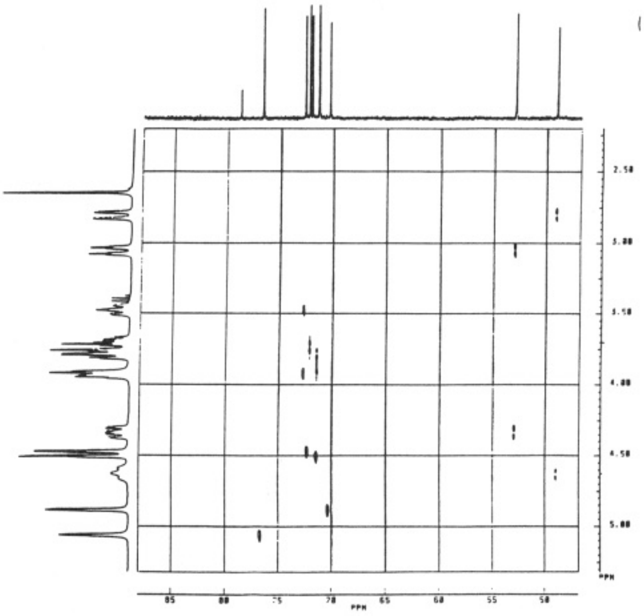

Figure 5. ^{13}C–^1H shift correlation spectrum of 1:Ba^{2+} in MeCN-d_3 at 5×10^{-2} M and 295 K.

The 2-D COSY and ^{13}C–^1H shift correlation spectra of 1:Ba^{2+} are shown in Figures 4 and 5. The C*H* and the CH_2 protons (identified by DEPT of the carbons to which they are directly bonded) that are cis to the carbonyl groups in 1:Ba^{2+} will reside most within the anisotropic conical deshielding zones of their neighboring carbonyl groups, and hence these protons will resonate at lowest field. Therefore, by assignment of the ^1H resonance at 5.06 ppm to the *C*H nuclei cis to the carbonyl (H2′ in Figure 3A,B), and that at 4.63 ppm to the CH_2 nuclei cis and closest to the carbonyl, inspection of the two-dimensional NMR spectra permits unambiguous assignment of all the other Fe*C*H and NCH_2CH_2 nuclei. However, in 1:Ba^{2+}, the eclipsed carbonyl groups coordinated to the complexed cation may be cis to the longer heterocyclic bridge (Figure 3A, structure A) or cis to the shorter heterocyclic bridge (Figure 3B, structure B). The NMR spectra indicate only one structural configuration to be present in solution. In order to

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[6] Hammond, P. J.; Beer, P. D.; Dudman, C.; Danks, I. P.; Hall, C. D.; Knychala, J.; Grossel, M. C. *J. Organomet. Chem.* **1986**, *306*, 367.

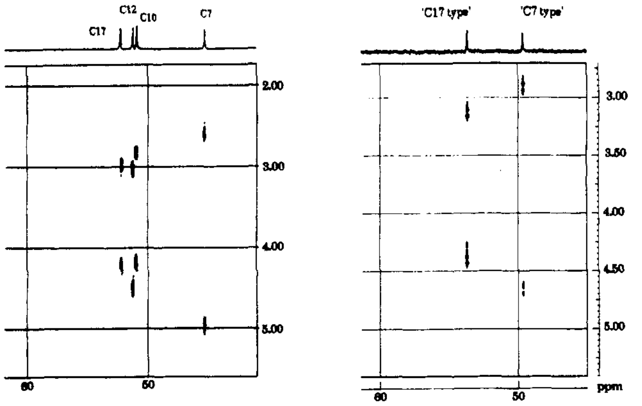

Figure 6. NCH_2 shift correlation spectra of (A, left) the host macrocycle 1 and (B, right) the complex 1:Ba^{2+}.

resolve this problem, examination of the ^{13}C–^{1}H shift correlation spectrum of the free host 1 proves useful. The cryptand 1 has no symmetry element, and four NCH_2 signals are observed with a shift correlation pattern to their bonded protons that is shown in Figure 6A. In 1 (see Figure 1), if we rotate the carbonyl group C6=O1 through 180° and impose a plane of symmetry through the atoms Fe and O3 and the midpoint of the bond C14–C15, then this "molecule" has carbonyl groups cis to the long heterocyclic bridge. The magnetic environment of C17 becomes equivalent to that of C12, as does that of C7 to C10. Therefore, for this theoretical molecule, we expect the four NCH_2 signals of 1 to coalesce to two signals with chemical shifts and correlation patterns similar to those of C12 and C10 in 1. Similarly, if we were to perform the same operations but instead rotate the carbonyl group C11=O2 through 180°, then the resulting theoretical molecule has eclipsed carbonyls cis to the shorter heterocyclic bridge and the magnetic environments of C12 and C10 become equivalent to those of C17 and C7, respectively. Therefore, we would anticipate that the four NCH_2 signals observed in 1 would reduce to two with chemical shifts and correlation patterns similar to those of C17 and C7. Figure 6B shows the NCH_2 shift correlation spectrum of 1:Ba^{2+}. Clearly this pattern resembles closely that of the *CH* nuclei of C17 and C7 in 1 but not those of C12 and C10 in 1. We conclude, therefore, that in the complex 1:Ba^{2+}, coordination of the Ba^{2+} cation is accommodated by eclipsed carbonyl groups and the metal cation occupies the smaller "side" of the host; i.e., the complex has the configuration structure B (Figure 3B). We can therefore analyze the NMR spectra of 1:Ba^{2+} with reasonable certainty, and the assignments are listed in Table II, where the atom identification nomenclature is that included in Figure 3B. Table II also includes the NMR data and assignments for the complexes 1:Be^{2+} and 1:Ca^{2+}, for which coordination is similarly by eclipsed carbonyls that are cis to the shorter heterocyclic bridge.

At first sight, this mode of complexation of the cations by 1 may seem surprising, since (a) the greater flexibility of the longer heterocyclic bridge allows scope for a less demanding stereochemical arrangement of potential donor atoms within the binding site and (b) the cation should prefer a potentially four-coordinate site (i.e. with carbonyls cis to the longer heterocyclic bridge, which contains two O atoms) rather than a three-coordinate site (i.e. short-side complexation). The structural chemistries of group II compounds are characterized by coordination numbers 4 (Be^{2+}) and 6 or higher (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}).[7,8]

Table II. ^{13}C and ^{1}H Chemical Shift Data (ppm) for the Complexes 1:M^{2+} in CD_3CN at ca. 5 × 10^{-2} M and 295 K[a]

	δ(^{13}C)				δ(^{1}H)		
atom	1:Be^{2+}	1:Ca^{2+}	1:Ba^{2+}	atom	1:Be^{2+}	1:Ca^{2+}	1:Ba^{2+}
C1	54.37	53.65	52.92	H1A	3.21	3.13	3.05
				H1B	4.44	4.42	4.34
C2	67.28	70.63	71.35	H2A	3.75	3.82	3.77
				H2B	3.75	3.90	3.94
C3	70.32	71.86	72.02	H3A	3.60	3.78	3.70
				H3B	3.76	3.78	3.76
C4	50.93	49.61	49.04	H4A	3.07	2.93	2.80
				H4B	4.56	4.65	4.63
C5	71.18	73.72	72.63	H5A	3.40	3.58	3.48
				H5B	3.83	4.02	3.92
C1′	76.90	78.90	78.77				
C2′	71.19	77.51	76.66	H2′	5.38	5.10	5.06
C3′	73.92	72.24	71.39	H3′	4.68	4.57	4.51
C4′	73.85	72.92	72.24	H4′	4.63	4.55	4.47
C5′	78.20	70.84	70.31	H5′	4.95	5.08	4.88
C=O	174.03	173.12	171.41				

[a] 1:Ca^{2+} was recorded at 333 K. ^{1}H data refer to multiplet centroids. From atom identification nomenclature, refer to structure B in Figure 3.

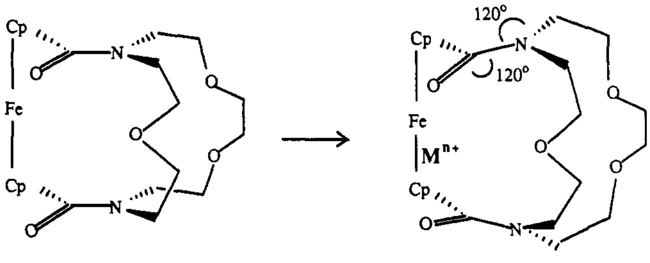

Figure 7. Stereochemical representation of eclipsed amides with cis carbonyl groups and of the molecular distortions relayed through the amide groups upon coordination of the metal cation (exaggerated for the sake of illustration; metallocene unit omitted).

However, strong complexation by hosts of this type has been shown to depend principally upon the presence of the *amide carbonyl* functions and not upon the presence of ether O atoms within the heterocyclic chains.[3] The preferential mode of complexation observed may be rationalized as follows. In 1, the Cp rings are spanned by one short and one long heterocyclic bridge. It is probable that the longer heterocyclic bridge experiences greater steric compression, since the inter-Cp ring separation in 1 is only 3.28 Å.[5] Upon complexation of the cation by 1, not only do the carbonyls become clipsed but also non-space-filling models indicate that the carbonyl groups can turn inward to the coordinated cation. In 1:M^{2+}, this distortion will be relayed through the amide groups placing the NCH_2 atoms that are trans to the carbonyl oxygen atoms at greater separation. An exaggerated representation of this situation is shown in Figure 7 in which the amide groups retain trigonal delocalized geometry and the Cp rings may also tilt inward in order to maintain conjugation with the carbonyl functions. Thus, coordination of the cation on the shorter side of 1 results in a relief of steric compression within the longer heterocyclic bridge. In effect, the 3-fold bridge asymmetry in 1 causes the molecule as a whole to behave as a "concertina", with the longer heterocyclic bridge acting as a coiled spring levering the amides so as to clamp the cation in the smaller cavity on the opposite side of the molecule. It is therefore the complex illustrated in Figure 3B that is the more thermodynamically stable. It would seem that matching the size of the cavity to the size of the cation or stereochemical

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(7) Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

(8) Bajaj, A. V.; Poonia, N. S. *Coord. Chem. Rev.* **1988**, *87*, 55.

placement of potential coordination donor atoms within the cavity are secondary considerations in this molecular design.

Variable-Temperature Studies. For the cations Be^{2+} and Ba^{2+} (the smallest and largest of the group II cations), their complexes with 1 are stable and soluble in MeCN (equimolar solutions at 295 K and up to 10^{-1} M) and have the structure shown in Figure 3B. By contrast, the complexes of the cations Mg^{2+} and Sr^{2+} with 1 are almost totally insoluble in MeCN. The complex with Sr^{2+} precipitates immediately. But, the complex 1:Mg^{2+} is apparently stable and soluble in MeCN for approximately 3 min (subsequent to mixing solutions of Mg^{2+} and 1 at 295 K and ca. 5×10^{-2} M). Thereafter, the contents of the solution precipitated almost totally with characteristic rapidity (ca. 30 s) to give a blood red crystalline product. Attempts to redissolve these precipitates in other solvents (polarity range pentane through methanol) were unsuccessful. Moreover, these crystalline products do not decomplex or decompose in the presence of water. Therefore, the stability of the Mg^{2+} and Sr^{2+} complexes suggests structures that are highly ordered due to an exact fit of the metal cation between the two carbonyls.

The cation Ca^{2+} is the middle-sized one of the group II cations, and its behavior with 1 differs from the other four examined in this work. The chemical shift data for 1:Ca^{2+} listed in Table II were assigned to the solution structure shown in Figure 3B, as were the complexes of Be^{2+} and Ba^{2+}. These data for 1:Ca^{2+} are for the predominant species (ca. 95%) formed shortly after mixing solutions of 1 and of Ca^{2+} at room temperature (at ca. 5×10^{-2} M). A minor species (ca. 5%) is also observed, with NCH_2 resonances at 50.44 and 52.52 ppm. We suggest that these resonances belong to the complex 1:Ca^{2+}, which has the solution structure shown in Figure 3A, i.e. with the cation Ca^{2+} coordinated by 1 via eclipsed amide carbonyls but which are cis to the longer heterocyclic bridge. Both stereochemical configurations of the complex are soluble. The complex observed as the minor component in solution is the kinetic product and has structure A (Figure 3A). Warming the solution to ca. 60 °C caused the minor component to disappear completely, and upon cooling, even to −40 °C, it did not reappear; i.e., the solution now contains only the thermodynamic product with structure B (Figure 3B). Preparing the solution at low temperatures increases the proportion of kinetic product observed while decreasing the proportion of thermodynamic product. Therefore, this suggests that for 1:Sr^{2+} the thermodynamic complex is formed directly and precipitation is immediate (i.e. the thermodynamic complex is also the kinetic product), whereas for 1:Mg^{2+} the thermodynamic product is formed via the kinetic product and precipitation is delayed. Variation in the kinetics of cryptate formation of alkali-metal cations with cryptands 222 and 221 has been observed previously.[9] The thermodynamic complex of 1:Mg^{2+} is not quite totally insoluble. The small amount in solution permitted low-resolution NMR data to be collected over a very long time. For this soluble component, two NCH_2 signals were observed with chemical shifts 49.69 and 53.68 ppm, consistent with the complex having structure B. Even at low temperatures, no evidence for 2:1 host–guest stoichiometries presented itself for any of the group II complexes, except possibly for Ca^{2+} at −40 °C.

Conclusions

A number of points with regard to the molecular design of bis(aminocarbonyl)ferrocene cryptand hosts capable of complexing alkaline-earth cations arise, and the factors that determine complexation behavior are revealed: (i) It is the amide carbonyl functions within the host molecular framework that are responsible for coordination of the group II cation. (ii) The host acts in effect as a bidentate ligand, with the carbonyl groups orientated cis, which introduces a plane of symmetry into the complex. (iii) Potential O-atom coordination by the heterocyclic polyether bridges is unimportant. (iv) The difference between the heterocyclic bridges within the host gives rise to a preferential stereochemical configuration for the complexes with group II cations. (v) The preferred mode of complexation arises because of steric compression and strains within the heterocyclic ring, which are relieved more by, and therefore determine, the stable stereochemical configuration of the host upon complexation. (vi) Kinetic as well as thermodynamic complexes are observed.

This selectivity in complexation behavior toward cations with a range of ionic radii manifests itself as follows: (i) The Be^{2+} complex is soluble and the cation is complexed on the shorter side (structure B). (ii) The thermodynamic complex with Mg^{2+} is almost totally insoluble and appears to form via an intermediate. (iii) For Ca^{2+}, complexation gives rise to both the kinetic product (structure A) and the thermodynamic product (structure B), both of which are soluble. (iv) Complexation with Sr^{2+} yields an insoluble product. (v) The Ba^{2+} complex is soluble and the cation is complexed on the shorter side (structure B); i.e., the behavior toward Ba^{2+} is the same as that toward Be^{2+}. (vi) No evidence for complexes with group I cations were observed.

Acknowledgment. We thank Fran Gallwey for collection of the NMR data and RTZ Chemicals Ltd., Rhone Poulenc Chemicals, and the SERC for financial support.

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