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90552-98-0; ethylene, 74-85-1; 2-butyne, 503-17-3; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (4 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Crystal Structure and Solution-State NMR Spectra of 1,1'-(1,4,10-Trioxa-7,13-diazacyclopentadecane-7,13-diylidicarbonyl)ferrocene Hydrate

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The crystal structure of the ferrocene-containing cryptand 1,1'-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diylidicarbonyl)ferrocene hydrate has been determined by X-ray crystallography. Crystals are orthorhombic, with $a = 8.575$ (6) Å, $b = 13.512$ (9) Å, $c = 17.734$ (11) Å, space group $P2_12_12_1$, and $d(\text{calcd}, Z = 4) = 1.53 \text{ g cm}^{-3}$. The structure was solved from the Patterson function and refined by least squares; $R_F = 0.056$ ($R_w = 0.058$). The cyclopentadienyl rings are almost parallel, the dihedral angle between their least-squares planes being 3.2 (6)°, with an inter-ring separation of 3.28 (2) Å. The ferrocene rings are rotated from the eclipsed conformation by only ca. 0.3° . The orientation of the carbonyls is *trans*, with substitution at the cyclopentadienyl rings staggered by ca. 71.7° . The amide π -bonding systems exhibit only slight distortions from planarity. The proposed structure in solution as determined by 2-D homo- and heteronuclear NMR techniques is consistent with the X-ray structure.

Introduction

Ferrocene-containing macrocycles have attracted considerable attention in recent years, and a range of ferrocene-containing cryptands has been synthesized in this laboratory.^{1,2} Their ability to complex metal cations offers the possibility for interaction between two metal centers. In particular, such compounds have yielded redox-active host molecules for selective recognition and binding of cations.^{3,4} Ferrocene-containing macrocycles may be crownlike, for which several structures are known to date,⁵⁻⁷ including one metal complex.⁸ Alternatively, they may be cryptandlike, for which one previous structure has recently appeared,⁹ together with that of a related compound,¹⁰ both of which are symmetric. Knowledge of the structural types for such macromolecular hosts is important, since it affords information on the factors determining the structure-binding relationship with guest molecules or ions. This paper reports the first solid-state crystal structure for an asymmetric ferrocene-containing

cryptand together with a detailed NMR analysis for the compound in solution.

Experimental Section

Synthesis. The title compound 1 was synthesized and purified by the general procedure outlined previously.¹ The product gave a satisfactory elemental analysis and relative molecular mass by mass spectroscopy. The crystal that proved suitable for X-ray studies was obtained by recrystallization from dichloromethane-ether.

Crystal Data, Structure Solutions, and Refinement. Crystal data for 1 were collected on a Picker four-circle diffractometer recently interfaced to an AT-TURBO 286 IBM-compatible microcomputer (full details to be published elsewhere) using Zr-filtered Mo $K\alpha$ radiation and pulse height analysis. The dark orange crystal was mounted in a sealed Lindemann glass capillary, since the crystals appear to be unstable in air. It was almost totally obscured by epoxy resin such that its dimensions could not be measured. Crystal data: $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_5\text{Fe}\cdot\text{H}_2\text{O}$, $M_r = 474.33$, $a = 8.575$ (6) Å, $b = 13.512$ (9) Å, $c = 17.734$ (11) Å, space group $P2_12_12_1$, $d(\text{calcd}, Z = 4) = 1.53 \text{ g cm}^{-3}$. Intensity data were collected in the θ - 2θ mode with a scan of 2° at 2° min^{-1} , with use of a modified version of a data collection program written by Grant and Gabe.¹¹ Only nonequivalent reflections were recorded to $2\theta_{\text{max}} = 50^\circ$, there being 1211 reflections out of 2072 having $I(\text{net}) > 2.5\sigma[I(\text{net})]$. Structure analysis was carried out by using the NRCVAX package.¹²

Phasing, starting from the Patterson function, was uneventful. After full-matrix non-hydrogen anisotropic refinement most hydrogen positions could be found on the ΔF map. Except for those in the water molecule, they were given theoretical positions ($\text{C-H} = 1.0$ Å) and isotropic temperature factors equivalent to

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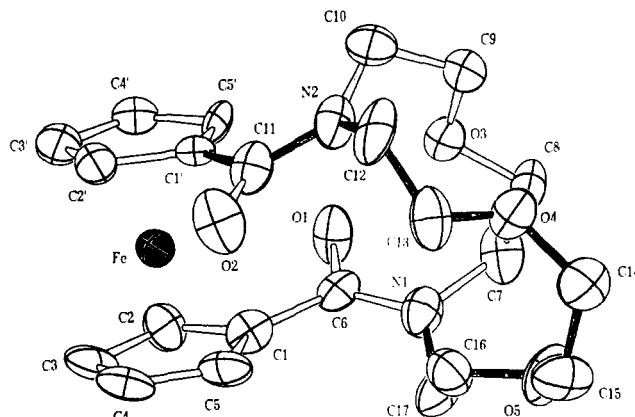
Table I. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors^a

atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
Fe	0.07460 (21)	0.39554 (13)	0.47804 (9)	2.49 (7)
N1	0.1061 (14)	0.6803 (8)	0.4301 (6)	3.5 (5)
N2	-0.1651 (15)	0.4517 (8)	0.2762 (6)	3.6 (5)
O1	0.3220 (9)	0.5886 (6)	0.4409 (5)	3.6 (4)
O2	-0.2816 (12)	0.3844 (9)	0.3760 (6)	5.0 (5)
O3	0.0875 (13)	0.6007 (7)	0.2879 (4)	4.1 (4)
O4	-0.3121 (13)	0.6438 (7)	0.2534 (6)	4.6 (5)
O5	-0.2288 (12)	0.7780 (7)	0.3751 (6)	4.4 (5)
O6	-0.4216 (19)	0.4965 (11)	0.4996 (7)	6.7 (7)
C1	0.1142 (12)	0.5351 (9)	0.5120 (7)	2.7 (5)
C2	0.2011 (16)	0.4681 (10)	0.5549 (7)	3.3 (6)
C3	0.1006 (16)	0.4053 (12)	0.5924 (6)	3.5 (6)
C4	-0.0547 (16)	0.4249 (11)	0.5699 (6)	3.4 (6)
C5	-0.0493 (14)	0.5092 (9)	0.5222 (8)	3.5 (6)
C1'	-0.0126 (14)	0.3639 (9)	0.3749 (6)	2.2 (5)
C2'	-0.0183 (17)	0.2789 (9)	0.4215 (7)	3.3 (6)
C3'	0.1349 (19)	0.2581 (10)	0.4458 (7)	3.8 (7)
C4'	0.2330 (17)	0.3265 (11)	0.4113 (7)	3.6 (6)
C5'	0.1403 (16)	0.3913 (11)	0.3700 (7)	3.0 (6)
C6	0.1878 (13)	0.6047 (10)	0.4592 (6)	2.6 (5)
C7	0.1740 (17)	0.7304 (10)	0.3657 (9)	3.9 (7)
C8	0.0965 (20)	0.7044 (9)	0.2933 (8)	3.9 (7)
C9	0.0206 (17)	0.5707 (10)	0.2190 (7)	3.9 (6)
C10	-0.0278 (23)	0.4642 (11)	0.2278 (7)	5.1 (9)
C11	-0.1590 (16)	0.4026 (11)	0.3428 (7)	3.5 (6)
C12	-0.3126 (22)	0.4719 (10)	0.2439 (9)	5.1 (8)
C13	-0.3939 (17)	0.5592 (11)	0.2755 (8)	4.3 (7)
C14	-0.3836 (18)	0.7367 (11)	0.2681 (8)	4.5 (7)
C15	-0.3833 (17)	0.7695 (12)	0.3465 (8)	4.6 (8)
C16	-0.1836 (17)	0.6952 (11)	0.4179 (8)	3.8 (6)
C17	-0.0364 (15)	0.7182 (9)	0.4604 (7)	3.5 (6)
H2	0.318 (19)	0.466 (12)	0.557 (8)	3 (4)
H3	0.134 (20)	0.353 (11)	0.630 (9)	3 (4)
H4	-0.150 (21)	0.387 (14)	0.585 (8)	4 (4)
H5	-0.141 (18)	0.544 (12)	0.500 (8)	3 (4)
H2'	-0.113 (20)	0.240 (12)	0.435 (9)	3 (4)
H3'	0.168 (20)	0.205 (12)	0.481 (10)	4 (4)
H4'	0.349 (18)	0.328 (11)	0.415 (8)	4 (3)
H5'	0.178 (21)	0.448 (12)	0.341 (9)	3 (4)
H7A	0.166 (21)	0.803 (13)	0.374 (10)	4 (4)
H7B	0.286 (21)	0.710 (14)	0.362 (10)	4 (4)
H8A	-0.010 (21)	0.735 (13)	0.291 (9)	4 (5)
H8B	0.160 (21)	0.732 (14)	0.250 (10)	4 (4)
H9A	0.097 (21)	0.577 (12)	0.177 (9)	4 (4)
H9B	-0.075 (24)	0.611 (13)	0.207 (9)	4 (4)
H10A	0.064 (25)	0.429 (13)	0.249 (11)	5 (5)
H10B	-0.050 (25)	0.439 (13)	0.175 (10)	5 (5)
H12A	-0.030 (25)	0.483 (14)	0.189 (11)	5 (5)
H12B	-0.383 (23)	0.414 (16)	0.254 (11)	5 (5)
H13A	-0.397 (20)	0.555 (12)	0.332 (9)	4 (4)
H13B	-0.504 (21)	0.562 (13)	0.255 (10)	4 (4)
H14A	-0.328 (21)	0.788 (13)	0.238 (9)	4 (4)
H14B	-0.496 (23)	0.734 (13)	0.251 (11)	4 (4)
H15A	-0.438 (23)	0.833 (13)	0.351 (9)	5 (4)
H15B	-0.440 (23)	0.718 (12)	0.378 (9)	5 (4)
H16A	-0.167 (21)	0.638 (12)	0.383 (9)	4 (4)
H16B	-0.269 (21)	0.678 (13)	0.455 (10)	4 (4)
H17A	-0.048 (21)	0.691 (11)	0.512 (11)	4 (4)
H17B	-0.026 (19)	0.791 (13)	0.463 (9)	4 (4)
HWA	0.610 (21)	0.458 (12)	0.462 (9)	6 (0)
HWB	0.595 (28)	0.526 (13)	0.470 (11)	6 (0)

^a For non-hydrogen atoms $B_{\text{iso}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j)$.

those of the atoms to which they were bonded. The coordinates of the water molecule hydrogen atoms were allowed to vary, but the isotropic temperature factors for both were kept at B_{iso} for the oxygen atom. The final least-squares cycle had $R_F = 0.056$ with $R_w = 0.058$ (based on counting statistics); $(\sum w(F_o - F_c)^2)/(N_o - N_c) = 1.90$. The crystal is one of a pair of enantiomorphs; reversing the signs of the fractional coordinates did not improve the F agreement ($R_F = 0.057$, $R_w = 0.061$). The difference is too small to decide on the absolute configuration of the molecule in the chosen crystal.

NMR Studies. High-resolution ¹H and ¹³C NMR data were obtained on a Bruker AM 360-MHz instrument using the CDCl₃

**Figure 1.** ORTEP²³ plot of non-hydrogen atoms showing 50% probability ellipsoids.**Table II. Bond Lengths (Å), with Estimated Standard Deviations in Parentheses**

Fe-C1	2.009 (12)	C1-C6	1.469 (18)
Fe-C2	1.999 (14)	C6-O1	1.215 (16)
Fe-C3	2.045 (10)	C6-N1	1.342 (17)
Fe-C4	2.010 (13)	C1'-C11	1.474 (19)
Fe-C5	2.024 (13)	C11-O2	1.229 (18)
Fe-C1'	2.021 (12)	C11-N2	1.356 (17)
Fe-C2'	2.031 (13)		
Fe-C3'	2.011 (14)	N1-C7	1.450 (19)
Fe-C4'	2.029 (15)	C7-C8	1.488 (20)
Fe-C5'	1.998 (13)	C8-O3	1.406 (15)
		O3-C9	1.410 (16)
C1-C2	1.399 (18)	C9-C10	1.505 (21)
C2-C3	1.381 (20)	C10-N2	1.468 (23)
C3-C4	1.416 (21)	N2-C12	1.415 (22)
C4-C5	1.419 (20)	C12-C13	1.480 (23)
C5-C1	1.456 (19)	C13-O4	1.396 (18)
C1'-C2'	1.416 (18)	O4-C14	1.422 (18)
C2'-C3'	1.410 (23)	C14-C15	1.458 (21)
C3'-C4'	1.391 (21)	C15-O5	1.423 (20)
C4'-C5'	1.391 (20)	O5-C16	1.407 (17)
C5'-C1'	1.365 (20)	C16-C17	1.503 (20)
		C17-N1	1.430 (19)

lines at 7.26 ppm for ¹H and 77.0 ppm for ¹³C as reference signals.

Results and Conclusions

X-ray Crystallographic Study. Final parameters are listed in Table I. Figure 1 shows a plot of the non-hydrogen atoms in the molecule and the atom-numbering scheme. Hydrogen atoms (except for those on water) have the same numbers as the atoms to which they are attached. Derived bond lengths, bond angles, torsional angles, and certain nonbonded distances are given in Tables II-V.

The molecules are hydrogen-bonded by the interleaving water molecules along the x axis: O1(x, y, z)...O6(x, y, z)...O2($x + 1, y, z$) with O1...HWB = 2.54 (23) Å and O2...HWA = 2.05 (16) Å, as shown in Figure 2. Amide oxygen to water hydrogen bonds are known in other crystal structures.^{13,14}

X-ray analysis confirms the predicted bond connectivity. The ferrocenyl group bridges the asymmetric diaza crown via amide bonds to the nitrogens. The carbonyl group containing atom O1 is cis to the shorter heterocyclic chain, and the carbonyl group containing O2 is cis to the longer chain. The trans orientation of the carbonyls, predicted by our earlier NMR studies,¹⁵ is confirmed. The ipso

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Table III. Selected Bond Angles (deg), with Estimated Standard Deviations in Parentheses

C5-C1-C2	106.8 (12)	C1-C6-O1	117.5 (11)
C1-C2-C3	109.1 (12)	C1-C6-N1	120.5 (11)
C2-C3-C4	109.6 (13)	O1-C6-N1	121.9 (12)
C3-C4-C5	106.7 (12)	C6-N1-C17	125.0 (11)
C4-C5-C1	107.4 (12)	C6-N1-C7	116.7 (11)
C5'-C1'-C2'	106.9 (11)	C17-N1-C7	118.2 (11)
C1'-C2'-C3'	107.9 (12)	C1'-C11-O2	118.2 (12)
C2'-C3'-C4'	107.3 (13)	C1'-C11-N2	122.9 (12)
C3'-C4'-C5'	107.7 (14)	O2-C11-N2	118.8 (12)
C4'-C5'-C1'	110.2 (13)	C11-N2-C10	122.3 (12)
		C11-N2-C12	118.8 (13)
		C10-N2-C12	117.2 (12)
C2-C1-C6	122.1 (11)		
C5-C1-C6	130.3 (11)	N2-C12-C13	114.9 (11)
C2'-C1'-C11	119.0 (12)	C12-C13-O4	108.0 (13)
C5'-C1'-C11	134.2 (12)	C13-O4-C14	117.1 (12)
		O4-C14-C15	116.2 (12)
N1-C7-C8	113.0 (11)	C14-C15-O5	111.5 (12)
C7-C8-O3	108.6 (10)	C15-O5-C16	112.6 (11)
C8-O3-C9	111.6 (9)	O5-C16-C17	109.8 (11)
O3-C9-C10	107.3 (10)	C16-C17-N1	117.1 (11)
C9-C10-N2	113.0 (12)		

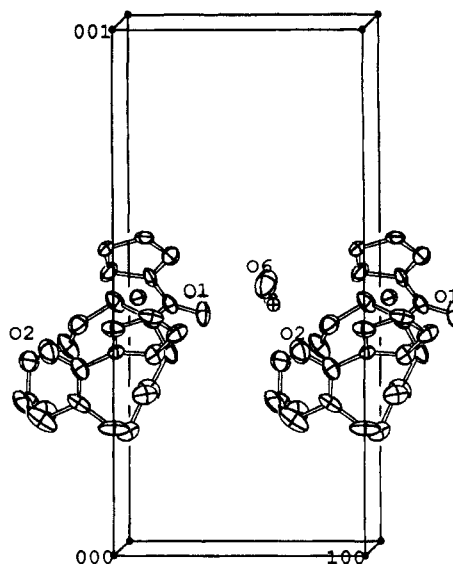
Table IV. Selected Torsion Angles (deg)^a

N1-C7-C8-O3	-50
C7-C8-O3-C9	-178
C8-O3-C9-C10	-163
O3-C9-C10-N2	+73
C9-C10-N2-C12	+79
C10-N2-C12-C13	-113
N2-C12-C13-O4	+69
C12-C13-O4-C14	+171
C13-O4-C14-C15	+74
O4-C14-C15-O5	+59
C14-C15-O5-C16	-99
C15-O5-C16-C17	-167
O5-C16-C17-N1	-101
C16-C17-N1-C7	-77
C17-N1-C7-C8	-79
O2-C11-N2-C10	-171
C1'-C11-N2-C10	+5
C1'-C11-N2-C12	+170
H2-C2-C1-C6	+6
C2-C1-C6-O1	+16
H2'-C2'-C1'-C11	+1
C2'-C1'-C11-O2	+25
O1-C6-N1-C7	+11
C6-N1-C7-H7B	-15
O2-C11-N2-C12	-6
C11-N2-C12-H12B	-37
O1-C6-N1-C17	-165
C1-C6-N1-C17	+19
C1-C6-N1-C7	+166

^a Estimated standard deviations are ca. 1°.**Table V. Selected Long Nonbonding Closest Contact Distances (Å), with Estimated Standard Deviations in Parentheses**

O1-H2	2.641 (15)	C1-C5'	3.189 (19)
		C2-C4'	3.196 (19)
O1-H7A	3.401 (15)	C3-C3'	3.288 (18)
O1-H7B	2.180 (15)	C4-C2'	3.303 (17)
		C5-C1'	3.282 (17)
O2-H2'	2.646 (17)		
		O1-HWB	2.54 (23)
O2-H12A	4.170 (19)		
O2-H12B	2.366 (16)	O2-HWA	2.05 (16)
N1-N2	4.733 (17)		

carbons, i.e. those to which the carbonyl substituents are directly bonded, are staggered by about 71.7°, a feature observed in the X-ray structure for the one previously reported ferrocene-containing cryptand.⁹

**Figure 2.** ORTEP plot of molecules *x*, *y*, *z* and *x* + 1, *y*, *z* showing hydrogen bonds from O1 and O2 to the water molecule.

Fe-C bond lengths cover the range 1.998 (13)-2.045 (10) Å (average 2.018 Å) and the intra-ring C-C bond lengths the range 1.381 (20)-1.456 (19) Å (average 1.404 Å). The internal bond angles within the cyclopentadienyl rings cover the range 106.7 (12)-110.2 (13)°. The closest inter-ring C-C contact distances cover the range 3.189 (19)-3.303 (17) Å, with the interplane distance between the cyclopentadienyl ring geometric centroids calculated as 3.280 (18) Å. Also, the cyclopentadienyl rings are not exactly parallel, having a dihedral angle of 3.2°. The inter-ring dimension is smallest on the side of the metallocene which is cis to that bridged by the smaller of the two heterocyclic bridges and largest on that side of the metallocene which is cis to the longer bridge. Therefore, the contraction due to the short bridge is relayed to the metallocene via the rigid amide groups.

The deviation from the eclipsed D_{5h} conformation of the metallocene ring for this nonsymmetric cryptand is small. Since the cyclopentadienyl rings are not regular pentagons, the angular twists between each of the five near-eclipsed carbon atom pairs range from +1.96 to -1.31°, with an average of +0.29°. The direction of inter-ring twist angle places the trans carbonyl groups at slightly closer separation than would be the case for an exactly eclipsed metallocene unit.

The conformation of the 15-membered heterocyclic ring is described by the torsion angles listed in Table IV. Three broad classes of torsion angle are evident, eight in the range 50.2-78.9°, three in the range 98.9-113.0°, and four in the range 163.4-177.7°.

In order to interpret the NMR spectra in detail (vide infra), the conformations about and through the amide functions revealed by the X-ray analysis prove informative. In the crystal the two amide ring fragments show different distortions from planarity. The stereochemistry of amide groups is well-known to reflect the resonance hybrid of two contributing canonical forms. One is the planar zwitterionic canonical form with extensive π -bond delocalization throughout the entire amide including enhanced C-N double-bond character. The other canonical form is non-planar with no delocalization of π -bonding and with no reduction in C-O double-bond character. Analysis of the four torsional angles which describe the planarity of each amide in 1 show that it is the amide containing the atoms O2 and N2 which is more planar. In this amide these four torsional angles are removed from planarity by 4.6-10.2°.

Table VI. ^{13}C and ^1H Chemical Shifts (ppm) for the Metallocene-Containing Cryptand 1, in CDCl_3

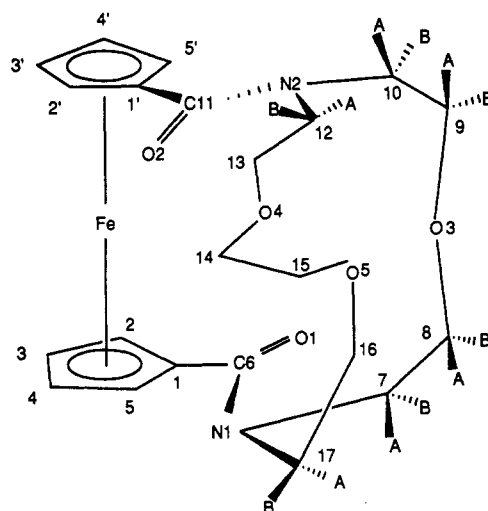
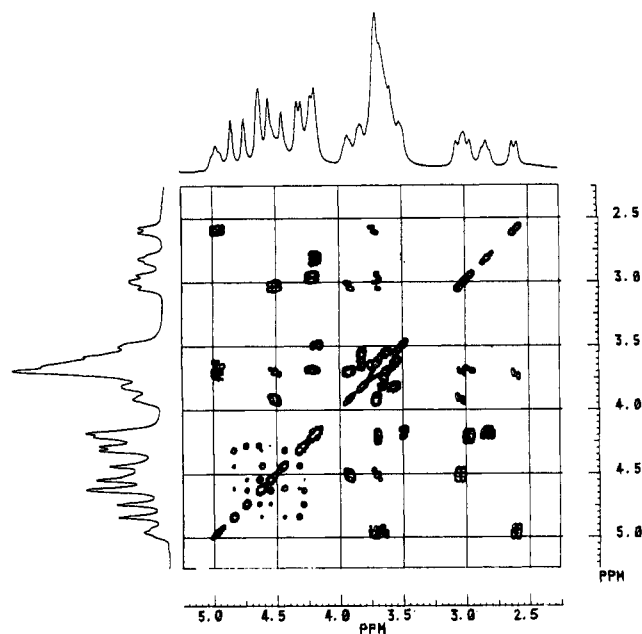
^{13}C nucleus	chem shift	^1H nucleus	chem shift
		H_2O	ca. 2.00 (broad)
C7	45.14	H7A	2.63 (d, $J = 14.1$ Hz)
		H7B	5.00 (m)
C10	50.77	H10A	2.85 (t, $J = 12.0$ Hz)
		H10B	4.23 (m)
C12	51.08	H12A	3.06 (d, $J = 15.9$ Hz)
		H12B	4.53 (m)
C17	52.09	H17A	3.00 (d, $J = 16.6$ Hz)
		H17B	4.27 (m)
C9	67.91	H9A	3.53 (d, $J = 9.5$ Hz)
		H9B	4.25 (m)
C14/C15	68.90	A,B pair	both at 3.68 (2) ^a
C13	69.28	H13A	3.70 ^a
		H13B	3.95 (m)
C16	69.59	A,B pair	both at 3.73 (2) ^a
C8	69.97	A,B pair	3.73 (2), ^a 3.76 (2) ^a
C14/C15	70.04	A,B pair	3.62 (m), 3.86 (m)
C3'	70.26	H3'	4.32 (s)
C4	70.47	H4	4.47 (s)
C3	70.81	H3	4.35 (s)
C4'	72.08	H4'	4.67 (s)
C5	72.58	H5	4.66 (s)
C2'	73.31	H2'	4.78 (s)
C2	73.56	H2	4.88 (s)
C5'	77.92	H5'	4.58 (s)
C1/C1'	78.63		
C1'/C1	78.79		
$2 \times \text{C}=\text{O}$	171.11, 173.49		

^a Multiplets overlap; uncertainty of multiplet centroid in parentheses.

For the amide containing the atoms O1 and N1, these four torsional angles are removed from planarity by 11.3–18.5°. Clearly the amide containing O1 and N1 has a conformation less favorable for π -bond delocalization throughout the entire amide, and therefore it is the carbonyl $\text{C6}=\text{O1}$ that has the greater π -bond character. However, both carbonyls have almost identical $\text{C}=\text{O}$ bond lengths.

The amide that is least stereochemically perturbed is, by contrast, the one with the shortest hydrogen bond between the carbonyl O atom and the interleaving water molecule. Therefore, the distortion from planarity of the amides is determined primarily by steric requirements imposed due to the asymmetry of the heterocyclic bridges. Upon dissolution of 1 in CDCl_3 the interaction of the water molecule with 1 is seen to persist, as evidenced by the broad resonance at ca. 2.00 ppm, which is integrated as two protons. This interaction in solution is probably intramolecular rather than intermolecular hydrogen bonding. However, since hydrogen bonding is secondary in determining the structure, the structure determined by solution NMR spectroscopy may be related closely to that observed in the solid.

NMR Study. NMR spectra for the title compound 1 have been reported previously.^{15,16} Additionally, the thermodynamic parameters for the fluxional motions within 1 have been determined by variable-temperature NMR studies.¹⁷ At the time an X-ray structure for 1 was unavailable and therefore assignments were to some extent open to question. The full NMR spectra for the compound 1 are listed in Table VI, together with our most recent assignments, given the advantage of 2-D homo- and heteronuclear NMR techniques and armed with the solid-state crystal structure for the compound. It is perhaps worth noting that the broad outline of the structure as revealed

**Figure 3.** Schematic illustration of 1 showing hydrogen atom stereochemistries and nomenclature.**Figure 4.** 2-D COSY spectrum of 1.

by these X-ray studies confirms most of the predictions made on the basis of these earlier NMR studies. This leads us to conclude that the solid-state X-ray structure bears a marked resemblance to that in solution. The stereochemistry of the protons within 1 is illustrated schematically in Figure 3, showing the class A methylenic hydrogens to be directed toward and class B hydrogens away from the interior of the heterocyclic ring.

The ^1H NMR spectrum reveals eight nonequivalent aromatic protons associated with the cyclopentadienyl rings. Therefore, the molecule possesses neither an axis nor a plane of symmetry. Of these aromatic resonances, the two most downfield must clearly belong to those protons cis to the carbonyl groups, i.e. H2 and H2'. This is because these two protons reside spatially within the anisotropic conical deshielding zones of their respective carbonyl groups. Examination of the crystal structure enables the most deshielded resonance at 4.88 ppm to be assigned to the proton H2. Two factors suggest this to be more deshielded than H2'. (1) The proton H2 is more coplanar with its neighboring carbonyl function and therefore resides in a more intense region of the deshielding zone. The torsion angles $\text{H2}-\text{C2}-\text{C1}-\text{C6}$ and $\text{C2}-\text{C1}-\text{C6}-$

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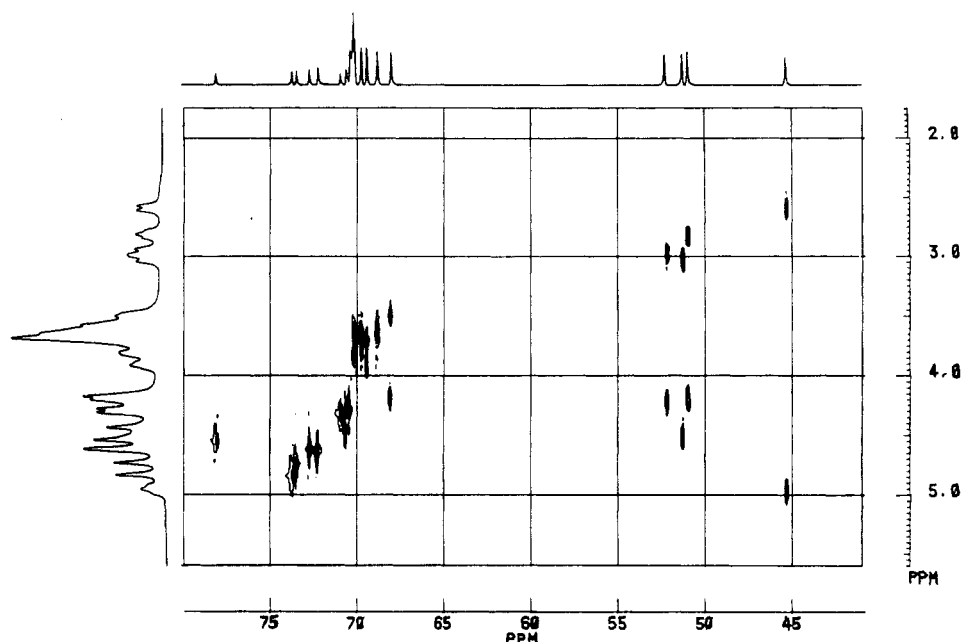


Figure 5. ^{13}C - ^1H shift correlation spectrum of 1.

O1 are $+5.9$ and $+16.1^\circ$, respectively, thus placing the H2 nucleus $+22.0^\circ$ out of the plane containing the $\text{C6}=\text{O1}$ carbonyl group. By comparison, the torsion angles $\text{H2}'\text{-C2}'\text{-C1}'\text{-C11}$ and $\text{C2}'\text{-C1}'\text{-C11}\text{-O2}$ are $+0.6$ and $+24.9^\circ$, respectively, placing the H2' nucleus $+25.5^\circ$ out of the plane containing the $\text{C11}=\text{O2}$ group. (2) As noted above, the amide carbonyl of greater π -bond character is $\text{C6}=\text{O1}$, which therefore has an anisotropic deshielding cone of greater magnitude.

Now that we have established the identity of the resonance associated with the proton H2, the 2-D COSY spectrum (Figure 4) reveals two weak couplings and one strong coupling, the latter to the resonance at 4.35 ppm. This is therefore established as that associated with H3. Further inspection of the 2-D COSY spectrum for H3 identifies H4, and hence H5, permitting complete unequivocal identification of the ring resonances. By similar logic the 2-D COSY spectrum establishes identities for the protons on the second cyclopentadienyl ring, given the resonance at 4.78 ppm to be H2'. No couplings are observed for any proton on one cyclopentadienyl ring with those of the other ring. The ^{13}C - ^1H shift correlation spectrum (Figure 5) permits ready identification of the cyclopentadienyl ^{13}C resonances, since the identities of the cyclopentadienyl ^1H nuclei are established. The identities of the ipso carbons C1 and C1' are not established, since they are not directly bonded to any proton; however, the DEPT spectrum clearly indicates these to be associated with the resonances at 78.63 and 78.79 ppm.

The ^{13}C resonance associated with the atom C5' is, in our experience, unusually downfield at 77.92 ppm. We have shown previously¹⁸ that the shielding of cyclopentadienyl ring ^{13}C nuclei for metallocene-containing cryptands of this type is directly related to the bonding electron density about the ^{13}C nucleus. Interestingly, the chemical shift, δ , for each cyclopentadienyl ring ^{13}C nucleus for 1, i.e. a measure of the extent of deshielding at each nucleus, corresponds closely to the rigidity of the ^{13}C atom as reflected in the magnitude of the value B_{150} , which for C5' is small at 3.0 \AA^2 .

For the methylene nuclei of the macrocyclic ring, the four high-field ^{13}C resonances are clearly those associated

with the nuclei NCH_2 . The ^{13}C - ^1H shift correlation spectrum clearly identifies the eight NCH_2 nuclei. Again, it is only by reference to the X-ray structure that the most deshielded proton may be established as H7B associated with the very low field multiplet centered at 5.00 ppm. Of the eight NCH_2 nuclei it is H7B that is closest to its neighboring carbonyl group and that is most coplanar with the $\text{C}=\text{O}$ bond. The through-space distance O1-H7B is 2.180 (15) \AA , and the torsion angles O1-C6-N1-C7 and C6-N1-C7-H7B are $+11.3$ and -14.8° , respectively, placing the atom H7B -3.5° out of the plane containing the carbonyl $\text{C6}=\text{O1}$. Given the identity of H7B, both 2-D COSY and ^{13}C - ^1H correlation spectra permit identification of H7A, the correlation spectrum identifies C7, the COSY spectrum gives the identities of H8A and H8B, and the correlation spectrum shows the identity of C8. Inspection of the crystal structure reveals the nucleus H12B to be the second closest and second most coplanar NCH_2 nucleus to its neighboring carbonyl. The distance O2-H12B is 2.366 (16) \AA , while the torsion angles O2-C11-N2-C12 and C11-N2-C12-H12B are -5.9 and -37.0° , respectively (net -42.9°). The nucleus H12B may therefore be assigned to the next most deshielded methylenic proton and associated with the resonance at 4.53 ppm. Given H12B, examination of the 2-D COSY and ^{13}C - ^1H correlation spectra identifies all six methylenic nuclei associated with positions 12 and 13.

The identity of the remaining two NCH_2 nuclei may be established by reference to earlier variable-temperature studies on 1.¹⁷ It is observed that at elevated temperatures the signal at 50.77 ppm coalesces with the C7 resonance at 45.14 ppm to the resonance midpoint, while that at 52.09 ppm coalesces with the C12 resonance at 51.08 ppm. Since the fluxional motion responsible for bringing these magnetic environments into equivalence is rotation of the amide carbonyls, then the resonance at 50.77 ppm must be that associated with C10, while that at 52.09 ppm is the signal for C17. Previous studies¹⁹⁻²² on secondary amides

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have shown the trans NCH₂ to resonate downfield with respect to the cis NCH₂ nucleus. For 1, the assignment of the cis, trans NCH₂ pair C7, C17 is consistent with this observation; however, for the pair C12, C10 it is not. This may reflect the nonplanarity of the amide functions. We are, however, comparing carbons in a five-atom chain with those in an eight-atom chain, and hence, conformational effects may override the difference expected for a cis/trans disposition of the carbon atoms. Given the identity of the nuclei C10 and C17, examination of the 2-D COSY and ¹³C-¹H correlation spectra permits assignment of the ¹³C resonances associated with the nuclei C9 and C16, together with the A, B proton pairs for all four carbons. No method exists to differentiate firmly between the more and the less shielded nuclei within each of these A, B proton pairs. However, the assignments given in Table VI are based upon the likely correlations with protons in comparable

structural sites in our earlier study of the related symmetric cryptand.¹⁸ No method is available to distinguish precisely between the nuclei of the 14,15-positions.

The solution structure is consistent with the solid-state X-ray structure. This detailed knowledge of the NMR spectrum permits us to study in solution the structural conformations for host/guest complexes of macrocycles such as 1 with metal cations. This is particularly important for examining the relationship between macrocycle design and their physical properties and potential applications in the field of selective metal cation recognition. To date, despite strenuous efforts, no crystals of host/guest complexes have been grown where the host is a cryptandlike ferrocene-containing macrocycle.

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Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Reactions of a Sulfido-Bridged Dinuclear Molybdenum Complex with Nitriles and Isonitriles under Hydrogen: Facile C≡N Bond Cleavage

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The dinuclear complex [(CpMo)₂(S₂CH₂)(μ-S)(μ-SH)]⁺X⁻ (X = SO₃CF₃, BF₄; Cp = C₅H₅; 1(X)) reacted with nitriles RCN under 1-2 atm of H₂ at 25-50 °C to form the new cationic complex [CpMo(S₂CH₂)(S₂CR)MoCp]⁺ and ammonia. The reaction has been characterized for HCN as well as for a series of alkyl- and aryl-substituted nitriles. Complex 1 reacted with isonitriles (RNC) and hydrogen under similar conditions to form the cationic complex [CpMo(S₂CH₂)(S₂CH)MoCp]⁺ and the primary amine RNH₂. The reactions were inhibited by excess acid. In order to probe the mechanisms of these reactions, the interactions of nitriles and isonitriles with 1 in the absence and presence of a protic acid and in the absence and presence of hydrogen have been studied. In the absence of hydrogen, 1 reacted with isonitriles to form [(CpMo)₂(S₂CH₂)(S₂CNH(R))]⁺ (2), but no reaction of 1 with nitriles was detected spectroscopically. Under similar conditions in the presence of excess protic acid, 1 reacted with n-butyl isocyanide to form [(CpMo)₂(S₂CH₂)(μ-S)(μ-SCH=NHBu)]²⁺ (4) and with acetonitrile to form [(CpMo)₂(S₂CH₂)(μ-S)(μ-SC(CH₃)=NH₂)]²⁺ (5). These S-H insertion products were identified by spectroscopic methods. The reaction of 4 and 5 with hydrogen appeared to involve carbon-sulfur bond hydrogenolysis; e.g., in the reaction of 5 with H₂, ethylammonium ion was identified as a product. The C-N bond cleavage reactions are proposed to involve the deprotonated forms of the insertion products 4 and 5, [(CpMo)₂(S₂CH₂)(μ-S)(μ-SCH=Nbu)]⁺ and [(CpMo)₂(S₂CH₂)(μ-S)(μ-SC(CH₃)=NH)]⁺. The former complex was tentatively identified by NMR spectroscopy. Reactions of these derivatives with hydrogen are proposed to lead to intramolecular S-H insertion products [(CpMo)₂(S₂CH₂)(S₂CH(NH₂Bu))]⁺ (6) and [(CpMo)₂(S₂CH₂)(S₂C(CH₃)NH₂)]⁺ (7). A precedent for this type of reaction has been characterized in a related molybdenum system. Complexes 6 and 7 are expected to eliminate BuNH₂ and NH₃, respectively, to form the final molybdenum products. The possible relevance of these reactions to the reductions of nitriles and isonitriles effected by the nitrogenase enzymes is discussed.

Introduction

We have been investigating the role of homogeneous molybdenum sulfido complexes in reactions that involve the activation of hydrogen and the reductions of carbon-heteroatom bonds. For example, a cyclopentadienylmolybdenum(IV) complex with nucleophilic μ-sulfide ligands, (CpMo(μ-S))₂S₂CH₂, has been found to catalyze the hydrogenation of C=N bonds in imines, isocyanates, and

isothiocyanates and of N=N bonds in azo compounds under 1-3 atm of H₂ at mild temperatures.¹ The active catalyst has been postulated to be a complex with one or two SH ligands, and a dinuclear Mo(III) complex with a μ-SH ligand was synthesized as a model for the catalytic

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