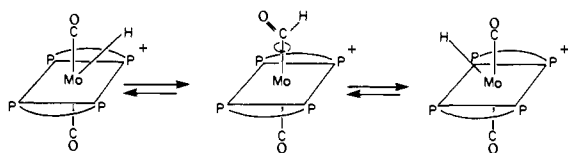


- (28) An alternate mechanism for the pairwise ^{31}P equilibration is one involving a formyl intermediate:



Metal formyls have been isolated [(a) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973); (b) S. R. Winter, G. W. Cornett, and E. A.

Thompson, *J. Organomet. Chem.*, **133**, 339 (1977); (c) C. P. Casey and S. M. Neuman, *J. Am. Chem. Soc.*, **98**, 5395 (1976)] and implicated in Fischer-Tropsch processes [(d) G. A. Mills and F. W. Seffgen, *Catal. Rev.*, **8**, 159 (1973)]. However, this mechanism does not account for the observed ^{13}C exchange.

- (29) (a) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974); (b) E. L. Muetterties, *Tetrahedron*, **30**, 1595 (1974).
 (30) G. A. Heath and R. Mason, personal communication quoted in G. A. Heath, J. Chatt, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074 (1974).
 (31) See C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977), and references cited therein.
 (32) (a) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943); (b) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958); (c) R. C. Fay, *Inorg. Chem.*, **3**, 348 (1964).

Cavities in Macrobicyclic Ligands and Complexation Selectivity.¹ Crystal Structures of Two Cryptates, $[\text{Na}^+ \subset 221] \cdot \text{SCN}^-$ and $[\text{K}^+ \subset 221] \cdot \text{SCN}^-$ ²

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Abstract: The crystal structures of two alkali metal ion cryptates, $[\text{Na}^+ \subset 221] \cdot \text{SCN}^-$ (I) and $[\text{K}^+ \subset 221] \cdot \text{SCN}^-$ (II), where $|221|$ is 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, have been determined. The crystals of I are monoclinic, $a = 13.258$ (5), $b = 12.906$ (5), $c = 12.645$ (5) Å, and $\beta = 94.77$ (3)°, space group $P2_1/c$. The structure was refined to an R_1 factor of 0.046 on 2590 independent nonzero reflections. The crystals of II are monoclinic, $a = 7.957$ (3), $b = 15.488$ (5), $c = 18.503$ (5) Å, and $\beta = 103.16$ (3)°, space group $P2_1/c$. The structure has been refined to an R_1 factor of 0.042 on 3077 independent nonzero reflections. In both compounds, the alkali cation is held inside the molecular cavity of the bicyclic ligand by ion-dipole interactions. In the potassium cryptate, the metallic ion also interacts with the thiocyanate anion. The selectivity of complexation is discussed in terms of structural parameters. The three-dimensional structures show that an enthalpic preselection is made by the ligand and an important entropic effect does the final selection.

It was proposed many years ago that ring chelates could be designed to select for metal ions on the basis of a compatibility between the cavity size of the ligand and the cation size.³ This expectation has been fulfilled in the last 10 years for the alkali and alkaline-earth metal cations.⁴ Many natural and synthetic ligands presenting high selectivities among these cations are now known and their properties are well documented.⁵

The most stable complexes known to date with the alkali and alkaline-earth metal cations are obtained with macrobicyclic ligands.⁶ Such ligands form inclusion complexes (cryptates) in which the metal cation is contained in a three-dimensional intramolecular cavity.⁷ Some of these bicyclic ligands display also very high selectivities for one alkali or alkaline-earth metal cation. For instance, ligand $|221|$ displays a peak selectivity for Na^+ . Its cavity size as evaluated on molecular models is ca. 1.1 Å, thus very close to the size of Na^+ . However, the thermodynamic quantities ΔG , ΔH , and ΔS involved in the complexation process in water show that the preference of ligand $|221|$ for Na^+ over K^+ is of entropic origin.^{6c} Thus the cavity radius-cation radius effect evaluated with molecular models does not give an accurate picture of the conformational parameters involved in the selectivity of complexation. In order to obtain a deeper insight into these parameters (equilibrium cavity, adaptability, and steric deformation of the ligand) we have studied the crystal and molecular structures of alkali metal cryptates with the bicyclic diazopolyether ligands presenting a peak selectivity for one cation. We report here the results obtained with the sodium and potassium salts: $[\text{Na}^+ \subset 221] \cdot (\text{SCN})^-$ (I) and $[\text{K}^+ \subset 221] \cdot (\text{SCN})^-$ (II) (see Figure 1).

Experimental Section

X-Ray Data Collection. Crystals were obtained by slow evaporation at room temperature of a methanol-butanol solution containing the metal thiocyanate and the ligand in a 1:1 mole ratio. Preliminary precession photographs showed monoclinic $2/m$ Laue symmetry. Systematic absences of $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$, identified the space group as $P2_1/c$ for both compounds. Subsequently, crystals were sealed in Lindemann glass capillaries and optically aligned on a PC2200-controlled Philips PW1100 diffractometer. Unit cell constants were determined from a least-squares analysis of the θ , χ , and ϕ angles of 19 reflections centered automatically, using graphite monochromated $\text{Cu K}\alpha$ radiation. Relevant crystal data are given in Table I.

The diffraction data were collected at room temperature ($20 \pm 1^\circ\text{C}$). The takeoff angle was 4° . The intensities of three standard reflections were measured after intervals of 90 min. They varied less than 1.25% for I and 4.04% for II. These values are obtained using the expression

$$\left[\frac{\sum_1^n (\chi_n - \bar{\chi})^2}{n-1} \frac{100}{\bar{\chi}} \right]^{1/2}$$

where χ_n and $\bar{\chi}$ are the number of counts of the n th measurement and the mean number of counts, respectively. The intensity data for the two compounds were reduced to relative squared amplitudes (F_o)² by application of standard Lorentz and polarization factors. Extinction and absorption effects were neglected for both data set.

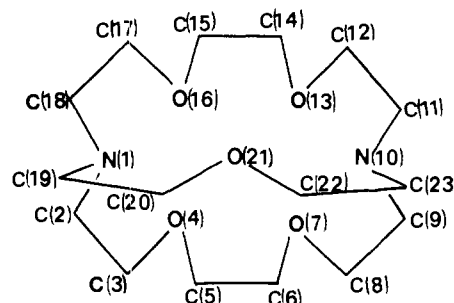
Both structures were solved by direct methods. The structure factors were first put on an absolute scale by calculating the statistical distribution of the E values for all the reflections. This resulted in 510 reflections with E values greater than 1.5 for I (408 for II). The most consistent set of signs for these reflections was calculated using the

Table I. Summary of Crystal Data and Intensity Collection

	compd I: $(C_{16}H_{32}N_2O_5) \cdot NaSCN$	II: $(C_{16}H_{32}N_2O_5) \cdot KSCN$
mol wt	413.51	429.62
<i>a</i>	13.258 (5) Å	7.957 (3) Å
<i>b</i>	12.906 (5) Å	15.488 (5) Å
<i>c</i>	12.645 (5) Å	18.503 (5) Å
β	94.77 (3)°	103.16 (3)°
<i>V</i>	2156.16 Å ³	2220.39 Å ³
<i>Z</i>	4	4
density (calcd)	1.274 g/cm ³	1.285 g/cm ³
density (obsd)	1.26 ± 0.03 g/cm ³	1.26 ± 0.03 g/cm ³
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
approximate crystal dimensions	0.25 × 0.25 × 0.25 mm	0.18 × 0.18 × 0.22 mm
μ	17.68 cm ⁻¹	31.82 cm ⁻¹
data collection method	θ -2 θ scan (2°/min along θ)	θ -2 θ scan (2°/min along θ)
background counts at both ends of the scan	7 s	7 s
θ limits	3-62°	2.5-60°
measured reflections	3733	3696
observed reflections	2590	3077
$F_o^2 > 3\sigma(F_o^2)$		
<i>F</i> (000)	888	920
scan range	0.80 + 0.28 tan θ	1.00 + 0.28 tan θ
<i>p</i> value	0.05	0.05
final <i>R</i> ₁ = $\Sigma(F_o - F_c)/\Sigma F_o $	0.046	0.042
final <i>R</i> ₂ = $[\Sigma w(F_o - F_c)^2/\Sigma w F_o]^{1/2}$	0.058	0.059

program MULTAN.⁸ The calculated phases were used to compute an *E* map, which revealed all the nonhydrogen atoms in I and II. Both structures were then refined by full-matrix least-squares techniques, the quantity minimized being $w(|F_o| - |F_c|)^2$, where the weights *w* were taken as $1/\sigma^2(F_o)$.⁹ For all structure factor calculations, the atomic scattering factors used were those calculated by Moore using Pepinsky's modifications.¹⁰ The effects of anomalous dispersion were included for the K, Na, S, and O atoms; the values of $\Delta F'$ and $\Delta F''$ are those given in ref 11.

Fourier difference maps computed at the end of isotropic refinement revealed electron density concentration close to the calculated positions for hydrogen atoms (C-H = 1 Å, X-C-H = 109.5°). These were introduced in all subsequent calculations with isotropic temperature factors fixed at 4 Å². A final series of least-squares refinements of positional parameters of all nonhydrogen atoms and anisotropic thermal parameters converged to *R*₁ = 0.046 for I, 0.042 for II, and *R*₂ = 0.058 for I and 0.059 for II. The final difference Fourier maps show no maxima greater than 0.26 e Å⁻³ for I, 0.39 e Å⁻³ for II. The final standard deviation of an observation of unit weight was 1.63 (I) and 1.85 (II).

**Figure 1.** Schematic representation and notation used in the $C_{16}H_{32}N_2O_5$ compound.

A listing of observed and calculated structure factor amplitudes based on the parameters of the final least-squares refinement and a table of positional and thermal parameters are available.¹² Bond distances and bond angles with estimated standard deviations calcu-

Table II. Intramolecular Distances (Å)

	I	II	I	II
M-N(CS)		2.776 (2)	C(11)-C(12)	1.498 (4)
M-N(1)	2.703 (3)	2.916 (2)	C(12)-O(13)	1.432 (3)
M-O(4)	2.491 (2)	2.871 (1)	O(13)-C(14)	1.421 (3)
M-O(7)	2.499 (2)	2.759 (2)	C(14)-C(15)	1.495 (4)
M-N(10)	2.591 (2)	2.897 (2)	C(15)-O(16)	1.434 (3)
M-O(13)	2.451 (2)	2.818 (1)	O(16)-C(17)	1.426 (3)
M-O(16)	2.519 (2)	2.702 (1)	C(17)-C(18)	1.496 (4)
M-O(21)	2.446 (2)	2.852 (1)	C(18)-N(1)	1.481 (3)
N(1)-C(2)	1.469 (4)	1.480 (3)	N(1)-C(19)	1.474 (3)
C(2)-C(3)	1.507 (4)	1.493 (4)	C(19)-C(20)	1.510 (4)
C(3)-O(4)	1.423 (3)	1.424 (3)	C(20)-O(21)	1.430 (3)
O(4)-C(5)	1.431 (3)	1.427 (3)	O(21)-C(22)	1.426 (4)
C(5)-C(6)	1.482 (4)	1.484 (5)	C(22)-C(23)	1.517 (5)
C(6)-O(7)	1.428 (4)	1.420 (3)	C(23)-N(10)	1.477 (3)
O(7)-C(8)	1.434 (4)	1.427 (3)	N-C	1.053 (6)
C(8)-C(9)	1.511 (4)	1.494 (5)	C-S	1.655 (5)
C(9)-N(10)	1.474 (4)	1.462 (4)		
N(10)-C(11)	1.479 (4)	1.479 (4)	N(1)-N(10)	4.944 (5)
				5.143 (4)

Table III. Selected Bond Angles (deg)^a

	I	II		I	II
N(1)-M-O(4)	67.0	60.6	N(1)-C(2)-C(3)	111.0	112.7
N(1)-M-O(7)	134.4	117.2	C(2)-C(3)-O(4)	107.3	107.4
N(1)-M-N(10)	138.1	124.4	C(3)-O(4)-C(5)	113.1	114.0
N(1)-M-O(13)	124.3	108.6	O(4)-C(5)-C(6)	108.6	107.6
N(1)-M-O(16)	67.0	62.5	C(5)-C(6)-O(7)	107.5	109.2
N(1)-M-O(21)	68.3	62.4	C(6)-O(7)-C(8)	113.7	113.8
N(1)-M-N		95.5	O(7)-C(8)-C(9)	112.0	109.4
O(4)-M-O(7)	67.4	59.8	C(8)-C(9)-N(10)	112.5	114.9
O(4)-M-N(10)	120.6	108.4	C(9)-N(10)-C(11)	111.5	109.6
O(4)-M-O(13)	154.0	160.7	C(9)-N(10)-C(23)	110.8	113.4
O(4)-M-O(16)	101.5	118.0	N(10)-C(11)-C(12)	112.0	114.0
O(4)-M-O(21)	101.0	79.9	C(11)-C(12)-O(13)	108.0	109.1
O(4)-M-N		83.3	C(12)-O(13)-C(14)	113.0	112.7
O(7)-M-N(10)	69.6	61.6	O(13)-C(14)-C(15)	108.5	108.5
O(7)-M-O(13)	97.6	121.5	C(14)-C(15)-O(16)	112.3	111.7
O(7)-M-O(16)	123.0	175.1	C(15)-O(16)-C(17)	113.8	114.4
O(7)-M-O(21)	121.4	89.5	O(16)-C(17)-C(18)	107.8	107.8
O(7)-M-N		95.7	C(17)-C(18)-N(1)	111.4	115.7
N(10)-M-O(13)	68.8	63.1	C(18)-N(1)-C(2)	111.1	109.2
N(10)-M-O(16)	136.3	122.9	C(18)-N(1)-C(19)	111.0	113.6
N(10)-M-O(21)	69.8	62.1	C(19)-N(1)-C(2)	112.2	111.4
N(10)-M-N		139.4	N(1)-C(19)-C(20)	111.8	112.7
O(13)-M-O(16)	68.1	62.2	C(19)-C(20)-O(21)	108.8	109.4
O(13)-M-O(21)	104.9	80.8	C(20)-O(21)-C(22)	111.7	111.2
O(13)-M-N		114.7	O(21)-C(22)-C(23)	107.9	109.6
O(16)-M-O(21)	115.6	94.5	C(22)-C(23)-N(10)	112.3	115.4
O(16)-M-N		79.5	C(23)-N(10)-C(11)	110.0	111.4
O(21)-M-N		156.9			

^a The estimated standard deviations are all less than 0.4°.

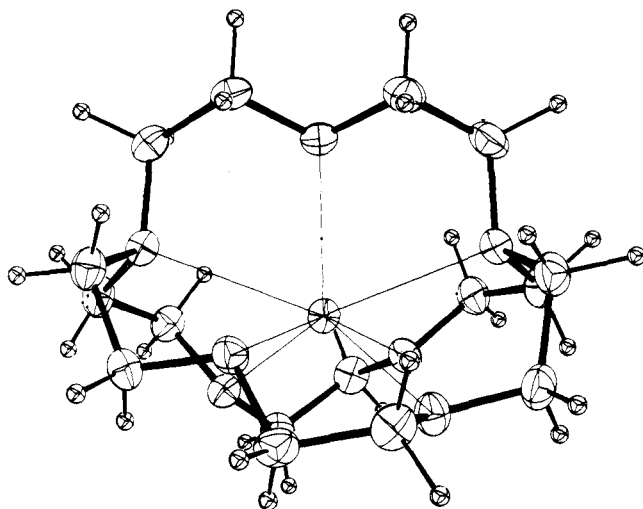


Figure 2. The $[\text{Na}^+ \subset 221]$ cation (30% probability ellipsoids).

lated from the full inverse matrix are presented in Tables II and III.

Results and Discussion

The three-dimensional structures of both cryptates are shown in Figures 2 and 3. In I and II the metallic cations are bound to all the heteroatoms of the ligand. The sodium ion occupies a central position, thus giving a bulky unipositive complex cation. The potassium ion lies in the cavity of the 18-membered ring of $[221]$ or slightly below in the opposite direction to O(21) rather than in the cavity of the bicycle. The coordination shell of the potassium ion is completed by a thiocyanate ion, whereas for sodium the solvation shell is completely replaced by the ligand. Thus, the crystal structure of the potassium cryptate consists of discrete molecules with

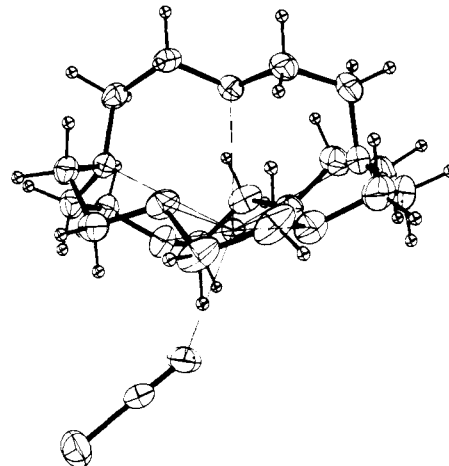


Figure 3. View of the $[\text{K}^+ \subset 221]\text{-SCN}^-$ molecule. Hydrogen atoms are represented by spheres of arbitrary size; thermal ellipsoids are drawn at the 30% probability level.

normal intermolecular approaches (the shortest S...C interaction is equal to 3.485 (2) Å) whereas that of the sodium cryptate consists of cations and anions. Studies of aqueous solutions of both cryptates have shown that their stabilities are not anion dependent.¹³ Most likely the thiocyanate anion is exchanged in aqueous solutions; the crystals were grown in methanol-butanol solutions.

The sodium ion in I is heptacoordinated. This involves an unusual geometry for a light alkali metal ion. The idealized structure is a bicapped tetragonal pyramid, derived from the tetragonal base-trigonal base (C_s symmetry)¹⁴ in which the three atoms N(1), N(10), and O(21) of the trigonal base are coplanar with Na. Their plane is orthogonal to the tetragonal base formed by the mean plane of O(4), O(7), O(13), and O(16), and bisects the angles O(4)-Na-O(16) and O(7)-Na-O(13). The symmetry of this polyhedron is near C_{2v} ; the

Table IV. Torsional Angles (deg)^a

A-B-C-D	I	II	A-B-C-D	I	II
N(1)-C(2)-C(3)-O(4)	66.0	67.9	C(19)-C(20)-O(21)-C(22)	-179.6	-165.4
C(2)-C(3)-O(4)-C(5)	173.0	176.7	C(20)-O(21)-C(22)-C(23)	-175.1	-170.6
C(3)-O(4)-C(5)-C(6)	177.0	177.5	O(21)-C(22)-C(29)-N(10)	-62.4	-62.8
O(4)-C(5)-C(6)-O(7)	-63.7	-67.0	C(18)-N(1)-C(2)-C(3)	84.8	95.3
C(5)-C(6)-O(7)-C(8)	176.0	172.6	C(19)-N(1)-C(2)-C(3)	-150.3	-138.4
C(6)-O(7)-C(8)-C(9)	-100.2	-174.2	C(2)-N(1)-C(18)-C(17)	-146.1	-172.4
O(7)-C(8)-C(9)-N(10)	-56.3	58.9	C(19)-N(1)-C(18)-C(17)	88.3	62.5
N(10)-C(11)-C(12)-O(13)	-60.6	-69.4	C(2)-N(1)-C(19)-C(20)	78.5	73.5
C(11)-C(12)-O(13)-C(14)	-172.2	177.9	C(18)-N(1)-C(19)-C(20)	-156.6	-162.7
C(12)-O(13)-C(14)-C(15)	-174.6	-175.7	C(11)-N(10)-C(9)-C(8)	-72.3	-172.7
O(13)-C(14)-C(15)-O(16)	55.3	64.8	C(23)-N(10)-C(9)-C(8)	164.8	62.1
C(14)-C(15)-O(16)-C(17)	78.6	97.7	C(9)-N(10)-C(11)-C(12)	155.4	161.6
C(15)-O(16)-C(17)-C(18)	169.4	-177.0	C(23)-N(10)-C(11)-C(12)	-81.2	-72.1
O(16)-C(17)-C(18)-N(1)	65.7	62.1	C(9)-N(10)-C(23)-C(22)	-83.4	-99.8
N(1)-C(19)-C(20)-O(21)	63.6	70.8	C(11)-N(10)-C(23)-C(22)	152.9	135.9

^a The estimated standard deviations are all less than 0.4°.

binary axis passes through O(21) and Na. The potassium ion in II is octacoordinated. The polyhedron is a bicapped distorted octahedron. It is formed by the oxygen atoms and the nitrogen of the thiocyanate anion. Here also, as in $|\text{Na}^+ \subset 221|$, N(1), K, N(10), and O(21) are nearly coplanar. The values of all the angles of the coordination shell are given in Table III. The symmetry of the polyhedron is near C_s .

In both I and II the ligand has the expected "in-in" conformation with the electronic pairs on the nitrogen atoms pointing toward the metallic cation. But the ligand is less symmetrical than the coordination polyhedra of the cations (neither C_{2v} nor C_s). The observed $\text{M}^+ \cdots$ heteroatom distances show an important dispersion compared to what has been found for other cryptates^{7a-c} (Table II). The average values for the $\text{M}^+ \cdots$ heteroatom bond distances are 2.91 ($\text{K}^+ \cdots \text{N}$) and 2.80 Å ($\text{K}^+ \cdots \text{O}$) in II; 2.64 ($\text{Na}^+ \cdots \text{N}$) and 2.48 Å ($\text{Na}^+ \cdots \text{O}$) in I. These values are thus fairly close to the sum of the appropriate radii in $|\text{K}^+ \subset 221|$, whereas the agreement is less satisfactory in $|\text{Na}^+ \subset 221|$. The calculated values, using the ionic radii of Pauling,¹⁵ revised by Ahrens¹⁶ and corrected for hepta- (I) and octacoordination (II) together with the standard packing radius of nitrogen (1.50 Å) and oxygen (1.40 Å) are 2.88 and 2.78 Å for $\text{K}^+ \cdots \text{N}$ and $\text{K}^+ \cdots \text{O}$; 2.50 and 2.40 Å for $\text{Na}^+ \cdots \text{N}$ and $\text{Na}^+ \cdots \text{O}$.

The $\text{N} \cdots \text{N}$ nonbonding distances are 4.944 (5) and 5.143 (4) Å in I and II, respectively. These values together with the $\text{N} \cdots \text{N}$ nonbonding distance found in $|\text{Co}^{2+} \subset 221|$ (4.20 Å)^{7k} indicate that the ligand has large flexibility. It is able to adapt its conformation and internal cavity to cations of fairly different dimensions.

The mean values of the bond lengths and angles in the ligand (see Tables II and III) are similar to those found in related ligands.^{7j} The values are O-C 1.43, N-C 1.48, C-C 1.50 Å; O-C-C 109, N-C-C 112 (I) and 114 (II), C-O-C 113, and C-N-C 111°. The O \cdots O and N \cdots O contacts in either I or II have standard values (see Table II). However, tensions are evident when considering the torsion angle values shown in Table IV. Some values correspond to configurations very different from the staggered one, especially around the nitrogen atoms. The ligand adapts its cavity to the dimension of the complexed cation. A rotation around C(8)-C(9) achieves this goal when Na^+ is replaced by K^+ .

The structural data obtained for I and II allow an estimation of the cavity radius R of ligand |221| in both compounds. The mean value of R is obtained from the following expression:

$$R = \left| \sum_n (d_{\text{M-O}_n} - 1.40) + \sum_{n'} (d_{\text{M-N}_{n'}} - 1.50) \right| / (n + n')$$

where $d_{\text{M-O}_n}$ and $d_{\text{M-N}_{n'}}$ represent the values of the metal-oxygen and metal-nitrogen distances, respectively. R is equal

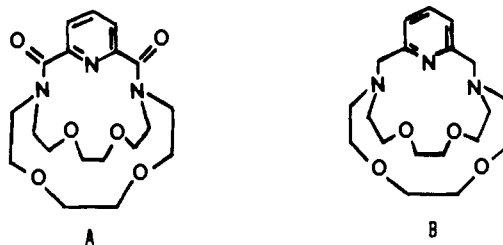
to 1.10 Å in I and 1.40 Å in II. Thus, in II the fit between the cavity and the part of the cation located inside is better than that between the cavity and the whole cation in I. A better fit between the cavity and cation and the presence in II of a metal-anion or -water bond should lead to a higher value of the enthalpy of complexation (ΔH_c) of ligand |221| with K^+ than with Na^+ , the other parameters being nearly constant.

These results are consistent with the calorimetric data published recently; the enthalpic variations during the complexation process of Na^+ and K^+ with |221| are equal to -5.35 and -6.80 kcal mol⁻¹, respectively.^{6c} Thus the preference of ligand |221| for Na^+ over K^+ is not due to cavity size effects but a favorable variation of the entropy of complexation.

Similar effects have been observed in the cryptates of ligand |222| with K^+ and Rb^+ . The flexibility of ligand |222| enables an excellent fit between cavity and cation in case of K^+ ($R = 1.38$ and calculated ionic radius $r_{\text{K}^+} = 1.38$ Å) and Rb^+ ($R = 1.50$ and $r_{\text{Rb}^+} = 1.52$ Å). These results are again consistent with the calorimetric data: the variations of enthalpy in complexation of K^+ and Rb^+ with |222| are almost identical, $\Delta H = -11.4$ kcal mol⁻¹ in $|\text{K}^+ \subset 222|$ and -11.8 kcal/mol⁻¹ in $|\text{Rb}^+ \subset 222|$.^{6c} Thus, the selectivity of |222| for K^+ over Rb^+ is again not due to cavity size effects, but to favorable entropy effects.

In the sodium cryptate of |222| the mean cavity radius R equals 1.21 Å, which is approximately 0.2 Å longer than the radius of Na^+ . In this case the fit between cavity of ligand |222| and Na^+ is rather bad. This is again reflected by the calorimetric data: $\Delta H_c = -7.4$ kcal mol⁻¹. Consequently, the preference of ligand |222| for K^+ over Na^+ is now due essentially to cavity size effects; the entropy term is not sufficiently important to reverse the selectivity pattern.

The flexibility of the ligand plays an important role.¹⁷ The pyridinophane cryptands A and B have cavity radii similar to that of |221|, but are more rigid. The rigidity introduced by a pyridinophane group affects the sodium more than the potassium complexes. The two ligands cannot adapt sufficiently their cavity to the size of the sodium cation. The entropy terms involved in the formation of the sodium complexes are no longer large enough to compensate the unfavorable enthalpy



variation. Effectively, the free energies of complexation, ΔG_c , are equal to -6.24 , -6.66 , -7.15 , and -6.51 kcal mol $^{-1}$ in $[\text{Na}^+ \subset \text{A}]$, $[\text{Na}^+ \subset \text{B}]$, $[\text{K}^+ \subset \text{A}]$, and $[\text{K}^+ \subset \text{B}]$, respectively.

In conclusion, the optimum dimension of the intramolecular cavity of ligand [221] is smaller than that of ligand [222]; the latter lies between 1.40 and 1.50 Å, that is, in between the radius of K^+ and Rb^+ , whereas the former has a value near to 1.30 Å, which is nearer the radius of K^+ than that of Na^+ . Selection being due to a cumulative effect of enthalpy and entropy of complexation the three-dimensional structures show that an enthalpic preselection is made by the ligand and an important entropic effect makes the final selection. Cavity size and ligand flexibility are major factors of preselection and can be designed a priori.

Supplementary Material Available: Listing of observed and calculated structural factors ($\times 10$) and positional atomic and anisotropic thermal parameters (18 pages). Ordering information is given on any current masthead page.

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Manganese(II) Porphyrin Oxygen Carriers. Equilibrium Constants for the Reaction of Dioxygen with Para-Substituted *meso*-Tetraphenylporphinatomanganese(II) Complexes

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Abstract: The reaction of molecular oxygen at -78 °C in toluene with a series of para-substituted *meso*-tetraphenylporphinatomanganese(II) complexes, $\text{Mn}^{\text{II}}(\text{T}(p\text{-X})\text{PP})(\text{L})$, containing an axial ligand, L, is described. Spectrophotometric titrations of toluene solutions of these complexes at -78 °C with molecular oxygen confirm the stoichiometry of the porphyrinatomanganese dioxygen complexes as $\text{Mn}(\text{T}(p\text{-X})\text{PP})(\text{O}_2)$. Equilibrium constants for the reaction $\text{Mn}^{\text{II}}(\text{T}(p\text{-X})\text{PP})(\text{L}) + \text{O}_2 \rightleftharpoons \text{Mn}(\text{T}(p\text{-X})\text{PP})(\text{O}_2) + \text{L}$ were determined for the series where X = Cl, F, H, CH_3 , and OCH_3 and L = pyridine. Log K (-78 °C, toluene) for the replacement of pyridine by O_2 ranged from -5.75 for $\text{Mn}^{\text{II}}(\text{T}(p\text{-OCH}_3)\text{PP})(\text{py})$ to -6.53 for $\text{Mn}^{\text{II}}(\text{T}(p\text{-Cl})\text{PP})(\text{py})$. (An error of ± 0.1 is estimated for the log K values; K has units of mol/L-Torr.) Fitting the observed values for the equilibrium constants to the Hammett equation ($-\log K$ vs. 4σ) gives a Hammett ρ value of -0.41 ± 0.08 . The effect of substituting the phenyl groups of the tetraphenylporphinatomanganese complex on the binding of molecular oxygen is discussed. Equilibrium constants for the replacement of L by O_2 at -78 °C in toluene for $\text{Mn}^{\text{II}}(\text{TPP})(\text{L})$, where L is a nitrogen, phosphorus, or sulfur donor ligand, are reported. Equilibrium constants (K_{L}) for the reaction $\text{Mn}^{\text{II}}(\text{TPP}) + 4\text{-cyanopyridine} \rightleftharpoons \text{Mn}^{\text{II}}(\text{TPP})(4\text{-cyanopyridine})$ were determined in toluene at 40.0, 23.0, and 0.0 °C. At 23.0 °C, the equilibrium constants for 4-cyanopyridine addition was determined as $\log K_{\text{L}} = 3.58$. A value for ΔH of -10.7 ± 0 kcal/mol for the reaction was calculated. Extrapolation of these data to -78 °C permits an estimate for the equilibrium constant at -78 °C for the oxygenation of four-coordinate $\text{Mn}^{\text{II}}(\text{TPP})$ as $K_{\text{O}_2} \sim 10^{2.1}$ Torr $^{-1}$.

Introduction

Until recently, the only synthetic metal complexes of biological interest that had been observed to reversibly bind molecular oxygen were those containing Fe(II) or Co(II) centers.¹

Recently, *meso*-tetraphenylporphinatomanganese(II) complexes of the form $\text{Mn}^{\text{II}}(\text{TPP})(\text{L})$,² where L represents a coordinating ligand, have been shown to act as reversible oxygen carriers in toluene solution at -78 °C.³