Helicity Interchange in Pendant Arm Tetraaza Macrocyclic Sodium(I) Complexes

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The temperature dependent ^{13}C NMR spectra of *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecanesodium(I) and its 2-methoxyethyl and (*S*)-2-hydroxypropyl analogues are consistent with helicity interchange of the approximately square antiprismatic isomers occurring much more rapidly than the exchange of Na$^+$ between the solvated and complexed states in methanol in the first two cases, and moderately more so in the last case.

A rare characterization of the isomerization and stereochemistry of alkali metal complexes is obtained from the temperature dependencies of the ^{13}C{^{1}H} NMR spectra (Fig. 1) of *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecanesodium(I) and its 2-methoxyethyl and (*S*)-2-hydroxypropyl analogues, [Na(thec12)]$^+$, [Na(tmec12)]$^+$ and [Na(*S*-thpc12)]$^+$, respectively, in ^{12}C-enriched [^{2}H$_4$]methanol. These spectral changes are consistent with helicity interchange ($\Delta \rightleftharpoons \Lambda$) occurring between two approximately square antiprismatic isomers as shown in Fig. 2 in which the helicity interchange, complexation and monomolecular decomplexation processes are characterized by k_{hi}, k_c and k_c', and k_d and k_d', respectively.

For the [Na(thec12)]$^+$ and [Na(tmec12)]$^+$ enantiomers, $k_c = k_c'$ and $k_d = k_d'$, and under slow exchange conditions the ring carbons *a* and *b*, which cannot be unequivocally identified with a specific carbon from our data, generate resonances at δ 50.29 and 48.98 (from external Me$_4$Si) for [Na(thec12)]$^+$ at 241.2 K, and δ 48.90 and 48.08 for [Na(tmec12)]$^+$ at 219.3 K, which coalesce to singlets as the temperature is increased and helicity interchange becomes more rapid. The magnetic environment of each of the equivalent pendant arm methylene carbons *c* and *d* in both complexes and the methyl carbon *e* in [Na(tmec12)]$^+$ is the same in each enantiomer and no coalescence phenomena are observed. {For [Na(thec12)]$^+$ the *c* and *d* resonances corresponding to the pendant arm –N*C*H$_2$– and –O*C*H$_2$– carbons appear at δ 54.89 and 57.35, respectively, at 241.2 K. For [Na(tmec12)]$^+$, the *c*, *e* and *d* resonances corresponding to the pendant arm –N*C*H$_2$–, methoxy and –O*C*H$_2$– carbons appear at δ 51.41, 57.83 and 68.34, respectively, at 219.3 K.}

This different behaviour of the ring and pendant arm carbon resonances also occurs for [Na(*S*-thpc12)]$^+$ (Fig. 1). Here the helicity interchange is between diastereoisomers ($\Delta S,S,S,S \rightleftharpoons \Lambda S,S,S,S$) which arise because the *S* chirality of each α-carbon is retained in each diastereoisomer. It might be anticipated that the diastereoisomers should experience sufficiently different magnetic environments to generate two sets of five ^{13}C resonances in the slow exchange condition. That only one set is observed at 277.7 K [ring carbons, –N*C*H$_2$–, –O*C*H(Me)– and –OCH(*Me*)– at δ 50.66, 48.81, 61.14, 62.34 and 20.08, respectively] indicates that the difference in magnetic environment is small and allows the characterization of an overall diastereoisomerization to which k_{hi} is assigned. {The observation of five ^{13}C resonances for both [La(*S*-thpc12)]$^{3+}$ and [Lu(*S*-thpc12)]$^{3+}$, which exhibit no coalescence over the temperature range 291.2–373.2 K in the first case, has been taken as evidence that only one diastereoisomer exists in solution,[1] but our observations on [Na(*S*-thpc12)]$^+$ indicate that this is not necessarily so.}

Stereochemistry similar to that shown in Fig. 2 has been observed in the solid state for [K(thec12)]$^+$, but in [Na(thec12)]$^+$ the hydroxy group of one of the pendant arms is not coordinated and Na$^+$ is seven-coordinate.[2,3] Such a seven-coordinate structure, if retained in methanol solution, could not produce the ^{13}C spectrum observed for [Na(thec12)]$^+$ in this study. A capped square antiprismatic structure of the type observed in the solid

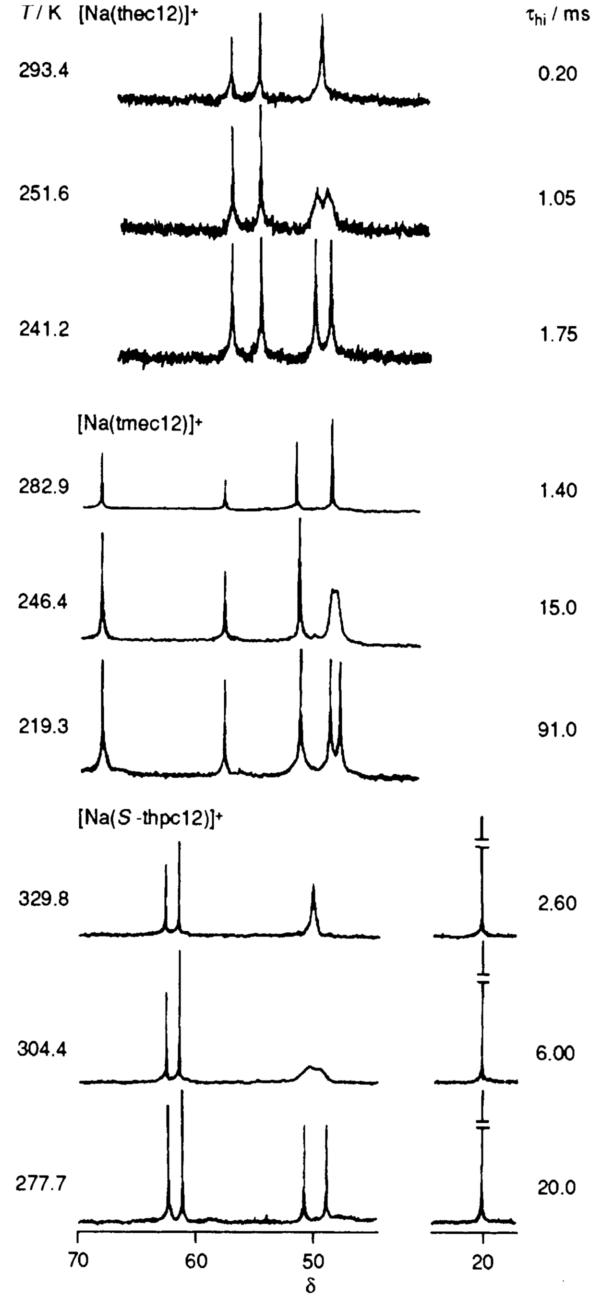

Fig. 1 Representative variable temperature ^{13}C{^{1}H} 75.47 MHz NMR spectra of [Na(thec12)]$^+$, [Na(tmec12)]$^+$ and [Na(*S*-thpc12)]$^+$ in ^{12}C-enriched [^{2}H$_4$]methanol where in each case a spectrum observed under conditions of slow, intermediate and fast helicity interchange is shown. The experimental temperature and the mean isomer lifetime, τ_{hi} ($= 1/k_{hi}$) are shown to the left and right of the figure, respectively.

Table 1 Rate parameters[a] for pendant arm tetraazamacrocyclic ligand sodium(I) complexes

Parameter	[Na(thec12)]$^+$	[Na(tmec12)]$^+$	[Na(*S*-thpc12)]$^+$
k_{hi}/s^{-1} (298.2 K)	7100 ± 220	1470 ± 90	125 ± 2
$\Delta H^‡$/kJ mol^{-1}	24.6 ± 0.5	31.4 ± 0.8	26.3 ± 0.5
$\Delta S^‡$/J K^{-1} mol^{-1}	−88.6 ± 1.8	−78.8 ± 3.6	−116.4 ± 1.8
k_d/s^{-1} (298.2 K)	209 ± 3[b]	<58	49 ± 1
k_c/dm^3 mol^{-1} s^{-1} (298.2 K)	7.08×10^6 [b]	$<9.2 \times 10^7$	3.1×10^6
log(K/dm^3 mol^{-1})[c] (298.2 K)	4.53 ± 0.04[b]	6.2 ± 0.1	4.8 ± 0.1

[a] For the kinetic parameters, the quoted errors are one standard deviation for the fit of k_{hi} and k_d to the Eyring equation. For log(K/dm^3 mol^{-1}), the quoted errors represent the largest difference between a single determination and the average of it and two others. For a single determination, the standard deviation for the fit of titration data to the stability constant equation did not exceed ±0.03 for log(K/dm^3 mol^{-1}). [b] Ref. 5. [c] At I = 0.05 mol dm^{-3} (Et_4NClO_4).

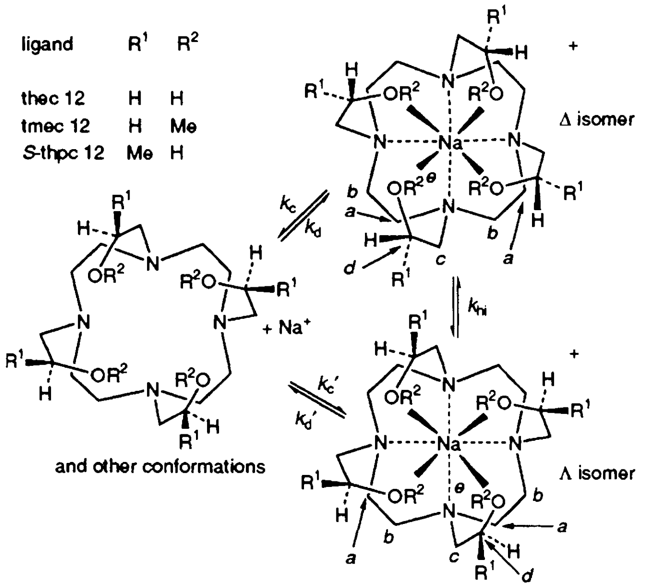

Fig. 2 Helicity interchange and Na$^+$ exchange in pendant arm macrocyclic sodium(I) complexes. The Δ and Λ assignments are based on the clockwise and anticlockwise helicity of the structure when viewed along the C_4 axis from the plane of the pendant donor atoms towards that of the macrocyclic ring.

state for nine-coordinate [Eu(thpc12)H_2O]$^{3+}$ (where thpc12 has either *R,R,R,S* or *S,S,S,R* configurations at the α-carbons) in which a water molecule is coordinated in the centre of the square face delineated by the four hydroxy groups,[1] could generate ^{13}C spectra similar to those in Fig. 1, but our study produced no evidence for nine-coordination.

The k_{hi} and k_d values (Table 1) were respectively derived through complete lineshape analysis[4] of the coalescence of ^{13}C resonances *a* and *b*, and of the ^{23}Na resonances (79.39 MHz) of solvated and complexed Na$^+$,[5] and k_c = k_dK where K is the potentiometrically determined stability constant. {For [Na(*S*-thpc12)]$^+$, a single intermolecular Na$^+$ exchange process is observed and the quoted k_d and k_c represent the weighted average of k_d and k_d', and k_c and k_c', respectively.} For [Na(thec12)]$^+$ and [Na(tmec12)]$^+$, k_{hi} is 34 and 25 times greater than k_d, respectively, consistent with helical inversion occurring predominantly through an intramolecular process in which all eight ligand donor atoms may remain bound in the transition state, but the possibility that one or more pendant arms become monodentate cannot be dismissed. For [Na(*S*-thpc12)]$^+$, k_{hi} is only 2.5 times greater than k_d, consistent with a significant proportion of helical inversion occurring through intermolecular Na$^+$ exchange. The differences in $\Delta H^‡$ and $\Delta S^‡$ for the three complexes are small, but their combination results in a 57 fold variation in k_{hi} at 298.2 K. The markedly decreased lability of [Na(*S*-thpc12)]$^+$ towards helical interchange by comparison with that of [Na(thec12)]$^+$ is largely attributable to the steric hindrance of the methyl group on each pendant arm. To a lesser extent this may also account for the decreased k_{hi} of [Na(tmec12)]$^+$, although such a steric effect is not readily distinguishable from the effect of changing from hydroxy to methoxy donor groups on bonding. [Preliminary studies indicate that helicity interchanges similar to those of the sodium(I) complexes occur in the lithium(I) and potassium(I) analogues.]

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