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Note

Cesium-133 nuclear magnetic resonance study of cyclogentiotetraose peracetate–cesium picrate complexation in non-aqueous solvents

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During the past two decades, alkali-metal complexation with macrocyclic ligands has been investigated by numerous authors[1] using several techniques. Multinuclear n.m.r. appears to be one of the most powerful techniques in this field of research.

In this paper we report on the complexation of cesium picrate[2] (CsPic) with cyclogentiotetraose peracetate[3] (**1**) by cesium-133 n.m.r.[4,5] in anhydrous acetone and nitromethane.

Cesium-133 n.m.r. spectra were recorded at 39.367 MHz with a Bruker AM-300 spectrometer; the ^{133}Cs chemical shifts were measured relative to the uncomplexed ^{133}Cs of the starting CsPic solution. All measurements were made at constant Cs^+ cation concentration (5mM); as the ligand concentration increased, the ^{133}Cs resonance shifted downfield. The variation of the ^{133}Cs resonance frequency at 323 K in acetone-d_6 as a function of the [**1**]/[Cs^+] molar ratio is shown in Fig. 1, which indicates a 1:1 complex formation.

$$\mathbf{1} + Cs^+ \rightleftharpoons \mathbf{1}\cdot Cs^+ \qquad (1)$$

The complexation constant K may be obtained from the variation of the observed chemical shift with the ligand/Cs^+ molar ratio, by a procedure already described by Popov and coworkers[6]. A least-square curve-fitting program calculates the complexation constant by successive iteration of K and δ_c (δ_c being the limiting chemical shift for the complexed ^{133}Cs), in order to obtain the best fit between experimental and theoretical data, as shown in Fig. 1. The estimated errors are ±0.10 for the log$K$ values, even though the computer fit indicates smaller errors.

At 323 K we obtained:

$\log K = 3.44 \pm 0.1$ in acetone,
$\log K = 3.32 \pm 0.1$ in nitromethane.

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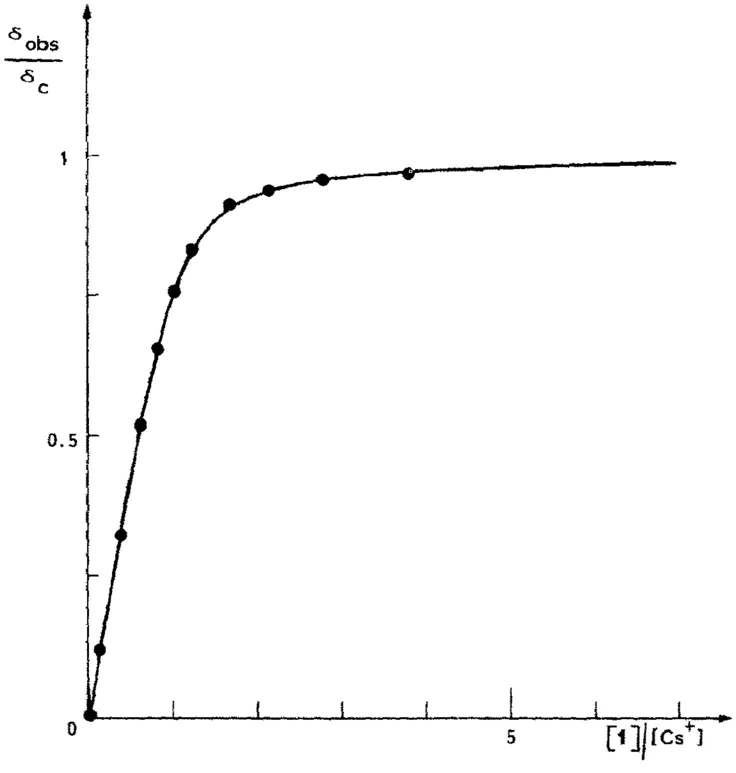

Fig. 1. Plot of normalized cesium-133 chemical shifts versus [1]/[Cs$^+$] molar ratio at 323 K in acetone-d_6. The solid line is a computer-fitted curve and dots are experimental points; (δ_{obs} and δ_c being the observed and the limiting chemical shifts, respectively).

In order to study equilibrium (*1*) at different temperatures, ^{133}Cs spectra were recorded for a mixture of **1** and CsPic (0.6/1 molar ratio) in acetone-d_6 solution. At 323 K we observed only one population-averaged signal (half-height linewidth: $\Delta\nu_{1/2}$ 127 Hz), indicating a fast exchange of the metal ion between the two cationic sites. Lowering of the temperature induced a line-broadening ($\Delta\nu_{1/2}$ = 473 Hz at 303 K: $\Delta\nu_{1/2}$ = 860 Hz at 293 K); the coalescence temperature was reached at 288 K. When the temperature was further lowered, two absorptions corresponding to the free and complexed ^{133}Cs species were observed. These two signals became narrow when the temperature was further decreased ($\Delta\nu_{1/2}$ Cs^+_{free} = 175 Hz, $\Delta\nu_{1/2}$ $Cs^+_{complexed}$ = 150 Hz at 263 K; $\Delta\nu_{1/2}$ Cs^+_{free} ~$\Delta\nu_{1/2}$ $Cs^+_{complexed}$ = 10 Hz at 203 K), as shown in Fig. 2.

This behavior indicates a slow exchange, on the ^{133}Cs n.m.r. time-scale, between the free and complexed cesium cation below 230 K.

From fully relaxed spectra recorded below the coalescence temperature, it is possible to calculate the complexation constant of equilibrium (*1*), at a given

TABLE I

LOGK VALUES FOR THE **1**–CsPic COMPLEX AT DIFFERENT TEMPERATURES

T(K)	*263*	*253*	*243*	*233*	*223*	*213*	*203*
log$K$	3.80	3.74	3.67	3.62	3.56	3.54	3.47

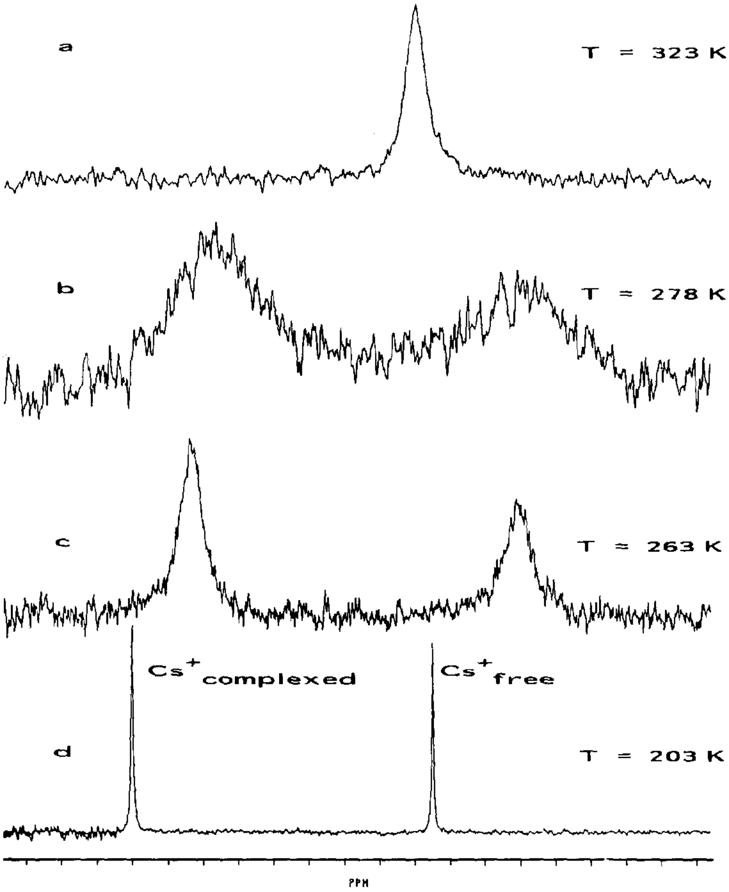

Fig. 2. Cesium-133 n.m.r. spectra of **1**/CsPic (0.6/1 molar ratio) in acetone-d_6 at various temperatures (the scale is graduated every 5 p.p.m.); *a*, rapid exchange; *b,c*, intermediate exchange; *d*, slow exchange.

temperature, by measuring the integral of each of the two signals (Table I).

According to Eq. (2),

$$\log K = -\frac{\Delta H^{\circ}}{2.3R}\frac{1}{T} + \frac{\Delta S^{\circ}}{2.3R} \tag{2}$$

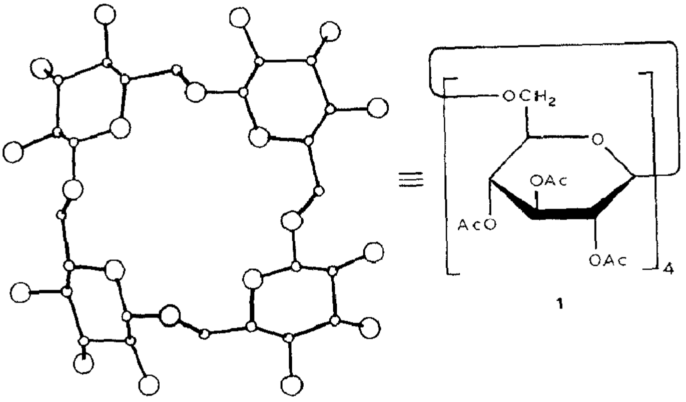

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Fig. 3. Schematic representation of cyclogentiotetraose (**1**); the acetate groups are not depicted.

and by plotting log$K$ = f(1/T) we can deduce the thermodynamic constants:

$$\Delta H^{\circ} = 1.2 \pm 0.3 \text{ kcal.mol}^{-1}$$
$$\Delta S^{\circ} = 21 \pm 2 \text{ cal.K}^{-1} \text{ mol}^{-1}.$$

From the ΔH° and ΔS° contribution to ΔG°, it may be concluded that the complex is entropy-stabilized in acetone.

Preliminary multinuclear (^{7}Li, ^{23}Na, ^{39}K, ^{87}Rb) n.m.r. experiments indicate that these four alkali cations give weaker complexes with **1** than cesium, in accord with the relative ionic diameter of cations (Li^+ 1.36; Na^+ 1.94; K^+ 2.66; Rb^+ 2.94; Cs^+ 3.34 Å) and the cavity (3.3 Å) of **1** obtained by molecular modeling[7] as shown in Fig. 3.

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