The self-assembly of a [2]pseudorotaxane of α-cyclodextrin by the slippage mechanism

Donal H. Macartney

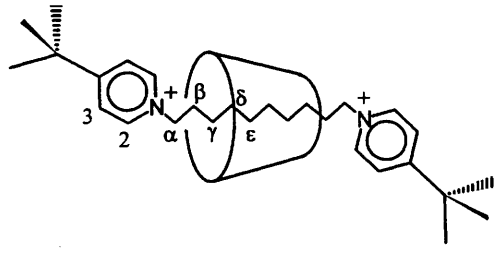
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

The kinetics and thermodynamics of the self-assembly of a [2]pseudorotaxane comprised of α-cyclodextrin and the 1,10-bis[1-(4-*tert*-butylpyridinium)]decane dication, by means of a slippage procedure, have been measured in aqueous solutions using ^{1}H NMR spectroscopy. The very slow threading of the α-cyclodextrin [$k_1 = (4.2 \pm 0.3) \times 10^{-4}$ s^{-1} at 25 °C] is preceded by a weak inclusion of the *tert*-butylpyridinium end group ($K_{CD} = 18 \pm 3$ dm^3 mol^{-1}). The dissociation of the [2]pseudorotaxane occurs with a rate constant of $(4.2 \pm 0.2) \times 10^{-6}$ s^{-1} at 25 °C, yielding a pseudorotaxane stability constant of $(1.8 \pm 0.2) \times 10^3$ dm^3 mol^{-1}.

Rotaxanes are supramolecular species in which a cyclic molecular bead is threaded by a linear chain bearing bulky end units, which prevent the complex from dissociating into its cyclic and linear molecular components.[1-14] The cyclodextrins, a series of cyclic oligosaccharides normally consisting of six (α-CD), seven (β-CD) or eight (γ-CD) α-(1→4)-linked D-(+)-glucopyranose units, have been frequently used as the cyclic component in rotaxanes in recent years.[5-11] A number of [2]pseudorotaxanes (end units not sufficiently bulky to prevent component dissociation) and [2]rotaxanes, based on α-cyclodextrin, have been reported in which threaded alkyl chains bear N-heterocyclic,[8,11] carboxylate,[9] cobalt amine[10] or pentacyanoferrate(II)[11] end units.

Several mechanisms for the formation of [2]rotaxanes have been identified.[2] The threading process involves the attachment of the bulky end units to the ends of a pre-threaded linear component (pseudorotaxane). In the clipping approach (not practical with cyclodextrins as the cyclic entity), the cyclic component is assembled around the linear portion, which already has the end groups in place. A third method, in which an end group dissociates, allowing threading by the cyclic bead (yielding a semirotaxane), and then reattaches, has been observed in this laboratory.[11] Self-assembling metal [2]rotaxanes of α-cyclodextrin, $[(NC)_5Fe\{R(CH_2)_nR'\cdot\alpha\text{-CD}\}Fe(CN)_5]^{4-}$ (n = 8–12, R = R′ = 4,4′-bipyridine,[11a,11b] R = R′ = pyrazine[11c] and R = pyrazine and R′ = 4,4′-bipyridine[11c]) have recently been prepared in aqueous solution by this mechanism. These complexes may also be formed rapidly and quantitatively by threading $[R(CH_2)_nR']^{2+}$ through α-CD and then complexing the N-heterocyclic rings with the bulky $[Fe(CN)_5]^{3-}$ end units.

An additional method of preparing rotaxanes, termed slippage,[12,13] has recently been utilized by Stoddart and coworkers.[14] When the cavity of the cyclic component and diameter of the end group(s) are closely matched in size, the threading of the cyclic component only occurs efficiently at elevated temperatures. The application of the slippage method to the synthesis of a [2] pseudorotaxane or [2]rotaxane of α-cyclodextrin would require an end unit, such as *tert*-butyl, which is comparable in size to the 5.5 Å diameter of the α-cyclodextrin cavity. In this study the results of a kinetic investigation of the thermally-promoted self-assembly and dissociation of the α-cyclodextrin [2]pseudorotaxane with the 1,10-bis[1-(4-*tert*-butylpyridinium)]decane dication, $[tbp(CH_2)_{10}tbp]^{2+}$, are described in terms of the slippage mechanism.



$[\{tbp(CH_2)_{10}tbp\cdot\alpha\text{-CD}\}]^{2+}$

Results and discussion

The threading of linear components of the type $[R(CH_2)_nR]^{n+}$ through the α-cyclodextrin cavity to form [2]pseudorotaxanes or [2]rotaxanes may be demonstrated by using ^{1}H NMR spectroscopy, as the symmetry-related proton resonances of the guest are split into pairs of peaks upon inclusion in the asymmetric cyclodextrin host. The addition of an excess of α-CD to the $[tbp(CH_2)_{10}tbp]^{2+}$ dication results in the very slow, spontaneous threading of the host by the guest molecule, as illustrated by the NMR spectra in Fig. 1.

The formation of the [2]pseudorotaxane (designated $[L\cdot\alpha\text{-CD}]^{2+}$) is also indicated by electrospray mass spectrometry. An aqueous solution of an equimolar (1×10^{-3} mol dm^{-3}) mixture of the two components, after equilibrating for 24 h, exhibited a peak at m/z = 692 (the [2]pseudorotaxane $\{L\cdot\alpha\text{-CD}\}^{2+}$, 88%) consistent with the species $[\{tbp(CH_2)_{10}tbp\cdot\alpha\text{-CD}\}]^{2+}$. In addition, a smaller peak was observed at m/z = 1178 ($L\cdot\alpha\text{-CD}^{2+}$, 5%) which may be attributed to a species containing $[\{tbp(CH_2)_{10}tbp\cdot 2\alpha\text{-CD}\}]^{2+}$, in which the terminal 4-*tert*-butylpyridinium group on the [2]pseudorotaxane is included in the cavity of a second α-CD host molecule.

The slippage process may be envisaged as occurring by first weak and reversible inclusion of the 4-*tert*-butyl group by the α-CD cavity [eqn. (1)], followed by a very slow passage over the

$$[tbp(CH_2)_{10}tbp]^{2+} + \alpha\text{-CD} \overset{K_{CD}}{\rightleftharpoons} [tbp(CH_2)_{10}\{tbp\cdot\alpha\text{-CD}\}]^{2+} \quad (1)$$

4-*tert*-butylpyridinium entity to finally position itself over the hydrophobic decamethylene chain to yield the pseudorotaxane [eqn. (2)].

Fig. 1 ^{1}H NMR spectra (400 MHz) of the formation of the [2]pseudorotaxane $\{tbp(CH_2)_{10}tbp{\cdot}\alpha\text{-}CD\}^{2+}$, recorded (*a*) 2 min, (*b*) 20 min, (*c*) 150 min and (*d*) 6 h after mixing $[tbp(CH_2)_{10}tbp]^{2+}$ (5.0×10^{-3} mol dm^{-3} after mixing) with α-cyclodextrin (5.0×10^{-2} mol dm^{-3} after mixing) in D_2O (0.10 mol dm^{-3} NaCl) at 25 °C

$$[tbp(CH_2)_{10}\{tbp{\cdot}\alpha\text{-}CD\}]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\{tbp(CH_2)_{10}tbp{\cdot}\alpha\text{-}CD\}]^{2+} \quad (2)$$

Upon initial addition of α-CD, the resonances for the *tert*-butyl methyl and the H_2 aromatic protons of the dication exhibit small (0.1 ppm) downfield shifts, while the H_3 protons shift upfield (0.05 ppm). These induced chemical shifts are very similar to those observed for the α-CD inclusion complex of the 1-methyl-4-*tert*-butylpyridinium cation, as described below, supporting an inclusion pre-equilibrium [eqn. (1)] prior to the slippage process.

The observed first-order rate constants for the slippage process increase with increasing α-cyclodextrin concentration, with the plots of k_{obs} *vs.* [α-CD] displaying curvatures towards rate saturation at high [α-CD] (Fig. 2). Assuming that k_{-1} is negligible with respect to k_1, the observed first-order rate constant may be expressed as follows [eqn. (3)].

$$k_{obs} = \frac{k_1 K_{CD}[\alpha\text{-CD}]}{1 + K_{CD}[\alpha\text{-CD}]} \quad (3)$$

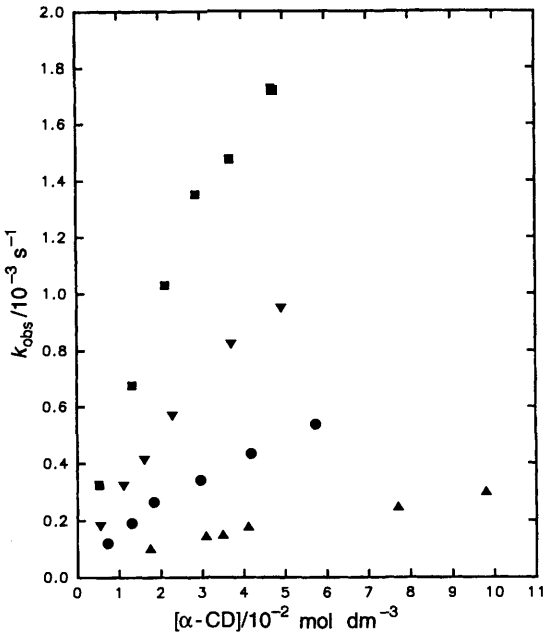


Fig. 2 Plots of the observed first-order rate constant for the formation of the [2]pseudorotaxane $[\{tbp(CH_2)_{10}tbp{\cdot}\alpha\text{-}CD\}]^{2+}$ *vs.* α-cyclodextrin concentration ($[tbp(CH_2)_{10}tbp]^{2+} = 5.0 \times 10^{-3}$ mol dm^{-3} after mixing) at ▲ 25 °C, ● 30 °C, ▼ 35 °C and ■ 40 °C

A double reciprocal plot of k_{obs}^{-1} *vs.* $[\alpha\text{-CD}]^{-1}$ at 25 °C (Fig. 3) yields a value of $k_1 = (4.2 \pm 0.3) \times 10^{-4}$ s^{-1} from the intercept, and $K_{CD} = 18 \pm 3$ dm^3 mol^{-1} from the ratio of the intercept to the slope. Similar plots have been constructed for the kinetics at 30, 35 and 40 °C (Fig. 3), yielding activation parameters of $\Delta H^{\ddagger} = 109 \pm 10$ kJ mol^{-1} and $\Delta S^{\ddagger} = +57 \pm 30$ J K^{-1} mol^{-1} associated with k_1. The inclusion stability constant K_{CD} was relatively constant (17–23 dm^3 mol^{-1}) over the temperature range investigated.

The stability constant for the inclusion of the 1-methyl-4-*tert*-butylpyridinium cation (which may represent the end unit of the linear component of the [2]pseudorotaxane) in α-cyclodextrin was determined to be 40 ± 3 dm^3 mol^{-1} by means of a ^{1}H NMR chemical shift titration (400 MHz) in D_2O (0.10 mol dm^{-3} NaCl) at 25 °C. Upon inclusion in the α-CD cavity the butyl proton resonance exhibits a limiting downfield shift of 0.12 ppm, while the N-methyl protons move upfield by only about 0.01 ppm. The H_2 ring protons shift downfield by 0.12 ppm, while the H_3 proton moves *ca.* 0.04 ppm in an upfield direction. This inclusion stability constant is smaller (likely due to the positive charge) but comparable to the stability constants determined for other 4-*tert*-butyl-substituted aromatic guests with α-CD; 85 ± 6 dm^3 mol^{-1} (for the 2:1 host–guest complex, $K_{2CD} = 20 \pm 2$ dm^3 mol^{-1}) for 4-*tert*-butylpyridine,[15] 83 dm^3 mol^{-1} for 4-*tert*-butylphenol,[16] and 47 ± 30 dm^3 mol^{-1} ($K_{2CD} = 29 \pm 8$ dm^3 mol^{-1}) for 4-*tert*-butyl-1,2-dihydroxybenzene.[17] The smaller value of K_{CD} obtained for the 4-*tert*-butyl substituent on the $[tbp(CH_2)_{10}tbp]^{2+}$ guest may result from a requirement that only certain orientations of the *tert*-butylpyridinium group in the α-CD cavity are favourable for the formation of the [2]pseudorotaxane.

The rate constant for the dissociation of the [2]pseudorotaxane into its linear and cyclic components was determined by adding an excess (5.3×10^{-3} mol dm^{-3}) of a competitive guest complex $[bpy(CH_2)_{12}bpy]^{2+}$ (bpy = 4,4′-bipyridine), to a solution of the preformed rotaxane (1.0×10^{-3} mol dm^{-3} of each component). The $[bpy(CH_2)_{12}bpy]^{2+}$ guest forms a [2]pseudorotaxane with α-cyclodextrin, with a stability constant of $(3.7 \pm 0.5) \times 10^3$ dm^3 mol^{-1} at 25 °C ($\Delta H^{\circ} = -35 \pm 4$ kJ mol^{-1}, $\Delta S^{\circ} = -50 \pm 10$ J K^{-1} mol^{-1}).[11b] The reaction was monitored by means of ^{1}H NMR spectroscopy by following the disap-

Table 1 Kinetic and thermodynamic parameters for the self-assembly and dissociation of the [2]pseudorotaxane [{tbp$(CH_2)_{10}$tbp·α-CD}]$^{2+}$ [a]

T/°C	$k_1/10^{-3}$ s^{-1}	K_{CD}/dm^3 mol^{-1}	$k_{-1}/10^{-5}$ s^{-1}	$K_1/10^3$ dm^3 mol^{-1}
25	0.42 ± 0.03	18 ± 3	0.42 ± 0.02	1.8 ± 0.2
30	0.00 ± 0.08	23 ± 4	0.81 ± 0.06	1.9 ± 0.2
35	1.8 ± 0.2	20 ± 4	1.8 ± 0.1	2.0 ± 0.3
40	3.8 ± 0.4	17 ± 3	3.7 ± 0.3	1.7 ± 0.2
45			5.3 ± 0.4	
50			11 ± 1	
55			17 ± 2	
ΔH/kJ mol^{-1}	109 ± 10	−7 ± 11	99 ± 3	−4±6
ΔS/J K^{-1} mol^{-1}	+57 ± 30	+1 ± 33	−17 ± 10	+48 ± 18

[a] In D_2O [I = 0.1 mol dm^3 (NaCl)].

pearance of the pair of doublets for the *tert*-butylpyridinium H_3 aromatic protons. The rate constant k_2 for the formation of the pseudorotaxane in eqn. (5) has been determined from pre-

$$[\{tbp(CH_2)_{10}tbp\cdot\alpha\text{-}CD\}]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [tbp(CH_2)_{10}tbp]^{2+} + \alpha\text{-}CD \quad (4)$$

$$[bpy(CH_2)_{12}bpy]^{2+} + \alpha\text{-}CD \underset{LO}{\overset{k_2}{\rightleftharpoons}} [\{bpy(CH_2)_{12}bpy\cdot\alpha\text{-}CD\}]^{2+} \quad (5)$$

liminary kinetic studies (using displacement experiments with Methyl Orange) to be *ca.* 20 dm^3 mol^{-1} s^{-1} at 25 °C.[18] This is considerably larger than the value (k_1K_{CD}) for the formation of [2]pseudorotaxane with the 4-*tert*-butylpyridinium dication, and as a result, the translocation of the α-CD between the two guests goes essentially to completion after several weeks. The value of k_{-1} is found to be (4.2 ± 0.2) × 10^{-6} s^{-1} at 25 °C, and a study of this reaction at several temperatures between 25 and 55 °C (Table 1) yielded activation parameters of $\Delta H^{\ddagger}$ = 99 ± 3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −17 ± 10 kJ mol^{-1}.

The stability constant K_1 for the [2]pseudorotaxane, with respect to its dissociated linear and cyclic components may be calculated from the formation and dissociation rate constants [eqn. (6)]. At 25 °C, the value is (1.8 ± 0.2) × 10^3 dm^3 mol^{-1},

$$K_1 = \frac{k_1K_{CD}}{k_{-1}} \quad (6)$$

with little dependence of the value on temperature (Table 1). This stability constant is in the range of values determined for a number of pseudorotaxanes of the type [{R$(CH_2)_{10}$R·α-CD}]$^{n+}$, where R is pyridine (2.2 × 10^3 dm^3 mol^{-1} at 5 °C),[8b] 4,4′-bipyridine [(1.5 ± 0.1) × 10^3 dm^3 mol^{-1} at 25 °C],[11b] pyrazine [(1.1 ± 0.1) × 10^3 dm^3 mol^{-1} at 25 °C[11c] and COO^- (1.4 × 10^3 dm^3 mol^{-1} at 30 °C).[9]

The results of this study indicate that the complementary sizes of the 4-*tert*-butyl substituent and the cavity of α-cyclodextrin result in a very slow threading of the cyclic component by the linear guest. This observation may be contrasted with [2]pseudorotaxanes of α-CD with [R$(CH_2)_n$R]$^{n+}$, where R is pyridine, 4,4′-bipyridine or pyrazine, which are formed upon mixing of the components. Using 4-isopropylpyridine as the end unit in the dicationic ligand also results in a rapid formation of the corresponding [2]pseudorotaxane [K_1 = (4.0 ± 1.1) × 10^3 dm^3 mol^{-1}], indicating a rather sharp break in the trend in the kinetics of the formation of these species.

The enthalpies of activation for the threading (109 ± 10 kJ mol^{-1}) and dethreading (99 ± 3 kJ mol^{-1}) processes in this study are very similar to one another, within experimental error. The differences in the rates of these processes, therefore, may be related to the entropies of activation. The positive entropy of activation for the threading of the α-CD (+57 ± 30 J K^{-1} mol^{-1}) likely results from the desolvation of the cationic pyridinium

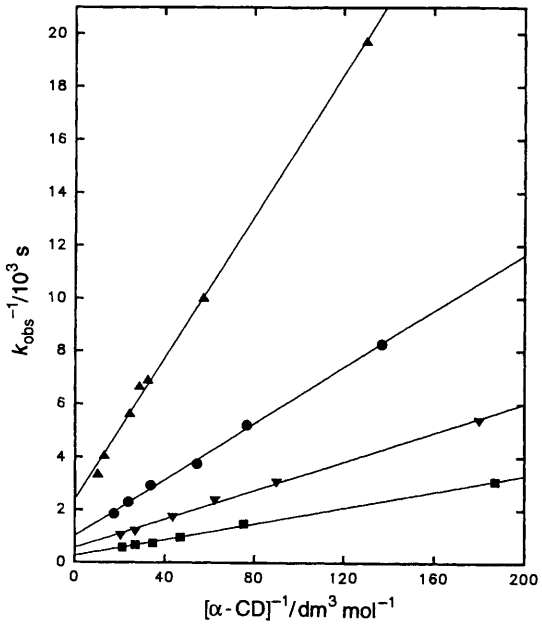


Fig. 3 Plots of k_{obs}^{-1} *vs.* [α-CD]$^{-1}$ for the formation of the [2]pseudorotaxane [{tbp$(CH_2)_{10}$tbp·α-CD}]$^{2+}$ at ▲ 25 °C, ● 30 °C, ▼ 35 °C and ■ 40 °C (reaction conditions as in Fig. 2)

group as it passes through the α-CD cavity. The unfavourable entropy of activation (−17 ± 10 J K^{-1} mol^{-1}) associated with k_{-1} would correspondingly result from resolvation of the pyridinium as it emerges from the α-CD cavity.

With [R$(CH_2)_{10}$R]$^+$ dications containing bulkier R end units, such as 3,5-dimethylpyridinium or quinuclidinium, formation of the [2]pseudorotaxane is not observed, even after prolonged heating.[18] Inspection of CPK models indicates clearly that these end groups are too large to thread through the α-cyclodextrin cavity. This work is currently being extended using a range of dicationic ligands, where R is a 3-substituted pyrazinium, 3- and 4-substituted pyridinium, trimethylphosphonium or trimethylammonium head group, to establish a correlation between rate constants for the threading/dethreading reactions and the steric nature of the end units.[18] In addition, linear components with chiral end units are being synthesized to investigate the possibility of chiral discrimination in the slippage process.

Experimental

Materials

α-Cyclodextrin (Aldrich) was dried at 80 °C under reduced pressure for at least 8 h prior to use.

1-Methyl-4-*tert*-butylpyridinium iodide. This was prepared by heating 4-*tert*-butylpyridine (Aldrich) with an excess of methyl iodide (Aldrich) in DMF at 50 °C for 24 h. After the solution had cooled, addition of diethyl ether resulted in the precipita-

tion of a crude product, which was recrystallized from ethanol–diethyl ether mixtures. Yield 65%, mp 122–124 °C (lit.,[19] 124–125 °C) (Found: C, 43.15; H, 5.65; N, 5.3. $C_{10}H_{16}NI$ requires C, 43.4; H, 5.8; N, 5.05%); $\delta_H(D_2O)$ 8.61 (2 H, d, H2), 8.03 (2 H, d, $J_{2,3}$ = 7.0 Hz, H3), 4.31 (3 H, s, N–CH_3), 1.40 (9 H, s, C–CH_3).

1,10-Bis[1-(4-*tert*-butylpyridinium)]decane dibromide hydrate. This was prepared by heating a mixture of 0.54 g (1.8×10^{-3} mol), 1,10-dibromodecane (Aldrich) and 0.90 g (6.7×10^{-3} mol) 4-*tert*-butylpyridine at 85 °C for 24 h in a mixture of dimethylformamide (3 cm^3) and benzene (2.5 cm^3). After the solution had cooled, a solid was precipitated using ether and recrystallized from ethanol–ether mixtures. Yield 85%, mp 116–118 °C (Found: C, 56.9; H, 8.0; N, 4.8. $C_{28}H_{46}N_2Br_2 \cdot H_2O$ requires C, 57.15; H, 8.2; N, 4.8%); $\delta_H(D_2O)$ 8.80 (4 H, d, H2), 8.07 (4 H, d, $J_{2,3}$ = 6.8 Hz, H3), 4.55 (4 H, t, $J_{\alpha,\beta}$ = 7.2 Hz, Hα), 1.99 (4 H, m, Hβ), 1.42 (18 H, s, –CH_3), 1.3 (12 H, m, Hδ-ε).

Physical measurements

The ^{1}H NMR kinetic measurements and chemical shift titrations were recorded on a Bruker AM-400 instrument, with the temperature of the NMR probe maintained at ±0.5 °C. In a typical kinetics experiment for the formation of the pseudorotaxane, a weighed amount of dried α-CD (5–100 mg) was added to a thermostatted solution of the $[tbp(CH_2)_{10}tbp]^{2+}$ ion (5.0×10^{-3} mol dm^{-3}) in D_2O containing 0.10 mol dm^{-3} NaCl. The mixed solution was transferred to a 5 mm NMR tube and spectra were collected at fixed intervals for at least four half-lives and then again after 10–15 half-lives (to determine $[L \cdot CD]_e$). The concentration of the pseudorotaxane formed from the guest (L) and host (CD) molecules ([L·CD]) was determined by integrating the H_2 aromatic resonances of the guest. Plots of $\ln\{([L \cdot CD]_e - [L \cdot CD]_0)/([L \cdot CD]_e - [L \cdot CD]_t)\}$ [the subscripts for [L·CD] refer to initial concentrations (0), at time t(t), and at equilibrium (e)] against *vs.* time were linear for at least three half-lives, with the slopes yielding rate constants (Fig. 2) with error limits in the range of 3–7% from linear regressions. For the kinetics of dissociation of the pseudorotaxane, a weighed amount (to give 5.0×10^{-3} mol dm^{-3}) of a competing guest, $[bpy(CH_2)_{12}bpy]Br_2 \cdot 0.5H_2O$,[7b] was added to a thermostatted solution of the [2]psedorotaxane (prepared by equilibrating 1.0×10^{-3} mol dm^{-3} solutions of α-CD and $[tbp(CH_2)_{10}tbp]^{2+}$ overnight). The ^{1}H NMR spectra were recorded at increasing time intervals (30 min to 12 h) over several days, with the NMR tubes thermostatted in a water bath between spectral data collection. Spectra recorded after several weeks indicated that the dissociation of the [2]pseudorotaxane was complete. The stability constant for the inclusion of the 1-methyl-4-*tert*-butylpyridinium cation in α-CD was determined from a ^{1}H NMR chemical shift titration as described previously.[17]

The electrospray mass spectrometry experiments were performed on a Fisons VG QUATTRO triple quadrupole mass spectrometer, with an electrospray interface. The samples were prepared in distilled water. Elemental analyses were performed by Canadian Microanalytical Services Ltd (Delta, BC).

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