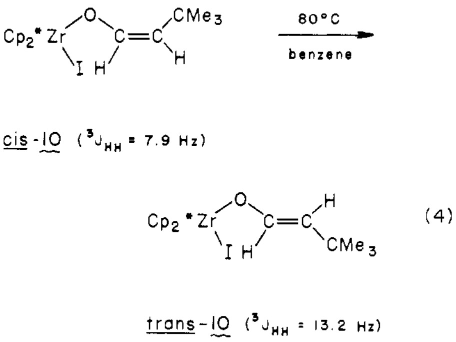

cis-10 ($^3J_{HH}$ = 7.9 Hz)

trans-10 ($^3J_{HH}$ = 13.2 Hz)

in a forthcoming article.[24] The reactivity of these and related ketene complexes is under further investigation.[25]

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Supplementary Material Available: Bond distances and angles (Table I) and labeling scheme (Figure 3) (2 pages). Ordering information is given on any current masthead page.

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Standard Enthalpies of Sublimation and Vaporization of 1,4,8,11-Tetraazacyclotetradecane and 1,4,8,11-Tetraazaundecane. Gas-Phase Macrocyclic Enthalpy

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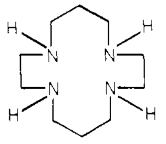
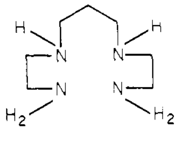
In an earlier paper,[1] the standard enthalpies of formation and solution of 1,4,8,11-tetraazacyclotetradecane (L_1) and 1,4,8,11-tetraazaundecane (L_2) were reported, and in the absence of experimental data, the values of the enthalpies of sublimation and vaporization, respectively, were estimated. A torsion-effusion, weight-loss apparatus has been constructed and calibrated.[2] This apparatus allows the determination of very low vapor pressures and has been used to evaluate the enthalpies of sublimation and vaporization of L_1 and L_2. The significance of these results is discussed below.



L_1



L_2

The apparatus is similar to that described by de Kruif and van Ginkel[3] and in general is suitable for compounds with vapor pressures between 0.1 and 10 Pa (see Figure 1). Typically, the effusion cell is loaded with approximately 200 mg of the compound mixed with silver turnings to promote thermal equilibrium. The apparatus is then evacuated to a pressure of 100 Pa, and in the torsion mode, the electric compensating circuit is set to zero. The pressure is then further reduced to below 0.1 Pa. In the weight-loss mode, the system is then left overnight for the balance to come to rest before measurements begin. After equilibration at each temperature, simultaneous resistance (temperature), voltmeter (torsion), or microbalance outputs are recorded on a 16K Pet microcomputer interfaced to the system. In the weight-loss mode, the readings are taken at precisely time intervals.

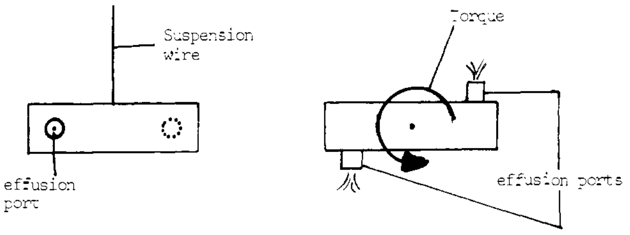


Figure 1. Sketch of effusion cell.

Table I. Vapor Pressure Data for L_1 and L_2

L_1		L_2	
T, K	*P*, Pa	*T*, K	*P*, Pa
352.26	0.040	332.38	0.61
359.99	0.107	335.38	0.81
360.29	0.110	335.53	0.84
361.40	0.131	339.37	1.24
367.31	0.254	341.99	1.645
368.84	0.309	343.65	1.93
371.87	0.425	346.69	2.60
372.34	0.453	347.66	2.87

Scheme I

$$\begin{tikzcd}
ML_2^{2+}(g) \arrow[d, "\Delta H^h(ML_2^{2+})"] & + & L_1(g) \arrow[d, "\Delta H^h(L_1)"] \arrow[r, "\Delta H_{gas}"] & ML_1^{2+}(g) \arrow[d, "\Delta H^h(ML_1^{2+})"] & + & L_2(g) \arrow[d, "\Delta H^h(L_2)"] \\
ML_2^{2+}(aq) & + & L_1(aq) \arrow[r, "\Delta H_{mac}"] & ML_1^{2+}(aq) & + & L_2(aq)
\end{tikzcd}$$

Dissolved air was removed from L_2, which is a liquid at room temperature, by repeated solidification and fusion of the sample under vacuum, and the sample was then transferred to the cooled cell as a solid.

In the weight-loss, or Knudsen mode, first formulated by Knudsen, the vapor pressure of the sample is given by the expression[4]

$$P = \frac{\dot{m}}{A}\left(\frac{2\pi RT}{M}\right)^{1/2}\frac{3l + 8r}{8r}\,\frac{1}{1 + 0.48r/2\lambda}$$

where P = pressure (Pa), $\dot{m}$ = rate of mass loss from cell (kg s^{-1}), A = cross-sectional area of the effusion port (m^2), M = molecular mass of the effusing species (kg), l = depth of the effusion port (m), r = radius of the effusion port (m), and λ = mean free path of effusing species = $(kT/\sqrt{2}\pi\sigma^2)(1/P)$ [σ = collision diameter (m)].

In the torsion-effusion mode, as the molecules effuse from the cell, the suspension wires are subject to a torque that is directly proportional to the vapor pressure of the sample. This torque is counterbalanced by passing a current through a coil mounted directly above the cell. The current required to bring the cell back to the zero point is determined as a voltage drop across a standard resistance. The vapor pressure is then given by

$$P = C'I$$

where C' contains only apparatus constants and is determined by

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using standard compounds and I is the measured compensating current.

Table I contains a representative set of results for each compound. The calculated values of P(torsion) and P(Knudsen) for a given compound agree to within 2% of each other, assuming a monomeric effusing species.

The standard enthalpy of sublimation (vaporization) was calculated by a least-squares fit of the experimental data to the Clausius–Clapeyron equation:

$$\ln P = A - \Delta H(\theta)/RT$$

where $\Delta H(\theta)$ = enthalpy of sublimation/vaporization at temperature θ, θ being the midtemperature of the range studied.

For L_1, ΔH_{sub} (362 K) = 31.3 ± 0.3 kcal mol^{-1}, and for L_2, ΔH_{vap} (340 K) = 23.5 ± 0.3 kcal mol^{-1}. Correction of these values to 298.15 K by means of the Kirchoff equation gives the following results:

$$\Delta H_{sub}{}^{\circ}(L_1) = 32.0 \pm 0.6 \text{ kcal mol}^{-1}$$

$$\Delta H_{vap}{}^{\circ}(L_2) = 23.9 \pm 0.6 \text{ kcal mol}^{-1}$$

The heat capacities needed for this correction are measured for solids and liquids by using a Perkin-Elmer DSC II instrument and estimates for the gaseous species from group values given by Benson.[4] A check with benzoic acid and naphthalene gave very satisfactory agreement for ΔH_{sub} with existing literature values. The values obtained for L_1 and L_2 compare favorably with the earlier estimates[1] of $\Delta H_{sub}(L_1)$ = 30.3 kcal mol^{-1} and $\Delta H_{vap}(L_2)$ = 21.6 kcal mol^{-1}.

The standard enthalpies of formation in the gas-phase are

$$\Delta H_f{}^{\circ}(L_1(g)) = 4.3 \pm 0.8 \text{ kcal mol}^{-1}$$

$$\Delta H_f{}^{\circ}(L_2(g)) = 0.0 \pm 0.8 \text{ kcal mol}^{-1}$$

From Scheme I it is apparent that the macrocyclic enthalpy, ΔH_{mac}, is made up of three terms:

$$\Delta H_{mac} = \Delta H_{gas} + [\Delta H^h(ML_1{}^{2+}) - \Delta H^h(ML_2{}^{2+})] + [\Delta H^h(L_2) - \Delta H^h(L_1)]$$

The third term, which we have evaluated in this work, $\Delta(\Delta H^h(L))$ = 5.2 kcal mol^{-1}, is almost identical with ΔH_{mac} for Cu(II)[6] and Ni(II)[7] systems, 4.7 and 4.9 kcal mol^{-1}, respectively. Providing the second term is small, as would be expected if there is only a small difference in the ionic radii of the complexes, we can conclude that the gas-phase macrocyclic enthalpy must also be small. In solution, the macrocyclic enthalpy is almost entirely due to the difference in hydration enthalpies of the uncoordinated ligands, a conclusion suggested some years ago by Margerum[8] using a less reliable value of ΔH_{mac} for the nickel complexes. It is also supported by recent work on similar tetrathia ligands,[9] which are very insoluble in water. In this case, one would expect little difference in the hydration enthalpies of the ligands, and indeed, ΔH_{mac} is close to zero. We are continuing this work with measurements on other tetraaza ligands.

Acknowledgment. We thank both SERC and NATO for financial support.

Registry No. 1,4,8,11-Tetraazacyclotetradecane, 295-37-4; 1,4,8,11-tetraazaundecane, 4741-99-5.

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Tropocoronands, a New Class of Metal-Complexing Macrocycles Derived from Aminotroponeiminates

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Nitrogen-containing macrocyclic ligands (coronands[1]) and their metal complexes have been widely employed in transition-metal chemistry and as models for bioactive molecules.[2] Recently, binucleating macrocycles have been studied to probe the unique properties of bimetallic centers.[3] Previous routes to coronands relied largely upon C–N bond formation either by template or direct Schiff base condensation reactions or by displacement by sodium sulfonamides.[4] The ability of 2-alkoxytroponeimines to undergo nucleophilic substitution reactions at the 2-position renders this system useful for the synthesis of macrocyclic ligands containing conjugated enamine imine moieties. Here we describe a novel family of easily synthesized tropocoronands that contain 2-aminotroponeimine units bridged by polymethylene, ether, or thioether chains, i.e., macrocycles **1** and **6** (Chart I). We also report the results of X-ray studies of five nickel(II) complexes that reveal the striking effect that varying the length of the linker chain has on the metal coordination geometry.

The synthesis of tropocoronand **1** is illustrated by the $-(CH_2)_4-$ case. 2-Chlorotropone[5] (16.3 mmol) and NEt_3 (18.1 mmol) in 30 mL of absolute EtOH was refluxed with **2** (n = 4) (9.2 mmol) in 15 mL of absolute EtOH for 6 h, the solvent was evaporated, and the residue was chromatographed on SiO_2 ($CHCl_3$–AcOEt) to give 1.51 g of bis(aminotropone) **3** (n = 4),[6] mp 126–127 °C ($CHCl_3$–AcOEt), 50% yield after recrystallization. Similar reaction of 2-chlorotropone with other α,ω-diaminoalkanes **2** (n = 2, 3, 5, 6), 3-oxa-1,5-diaminopentane,[7] or 3-thia-1,5-diaminopentane[8] gave corresponding bis(aminotropones) **3** in ca. 50% yield.

The carbonyl carbons of aminotropones **3** were activated by conversion to imines **4**. Bis(aminotropone) **3** (n = 4) (1.43 mmol) and HMPA[9] (2 g) in dry $CHCl_3$[10] were refluxed with Et_3OBF_4[11]

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