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:

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

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

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 $\Delta H_{\mathrm{sub}}(L_1)$ = 30.3 kcal mol^{-1} and $\Delta H_{\mathrm{vap}}(L_2)$ = 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:

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

The third term, which we have evaluated in this work, $\Delta(\Delta H^{\mathrm{h}}(L))$ = 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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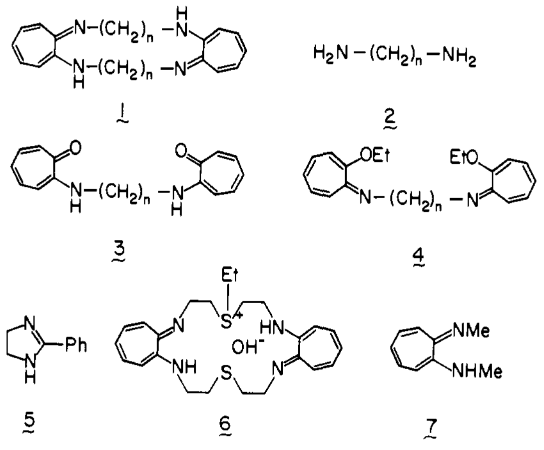
Table I. Selected Structural Features of Nickel(II) Tropocoronand Complexes

ligand	$(Ni–N)_{av}$, Å	θ,[a] deg	ϕ,[b] deg	N–Ni–N,[c] deg	N–Ni–N′,[d] deg
1 ($n = 3$)	1.863 (3)	8.33	14.7, 16.1	82.4 (1)	97.2 (1)
1 ($n = 4$)	1.882 (1)	28.9	4.2, 8.4	82.3 (1)	100.9 (1)
1 ($n = 2$)–O–($n = 2$)	1.946 (2)	74.5	7.6, 7.6	80.5 (1)	117.6 (1)
1 ($n = 5$)	1.949 (6)	70.1	7.6, 8.6	81.6 (2)	115.3 (3)
1 ($n = 6$)	1.950 (2)	85.2	3.4, 6.7	80.4 (1)	123.0 (1)

[a] Dihedral angle between N1–Ni–N2 and N3–Ni–N4 (see Figure 1). [b] Dihedral angles between N–Ni–N and troponiminato ring. [c] Average bond angle within the troponiminato chelate ring. [d] Average bond angles between two troponiminato rings.

Chart I



(7.2 mmol) for 18 h under N_2, the mixture was extracted with H_2O, and the aqueous extract was made alkaline with 5% Na_2CO_3 and extracted with $CHCl_3$ to yield the unstable oily imine **4** ($n = 4$) contaminated with HMPA, ca. 440 mg. This mixture was dissolved in 150 mL of EtOH, treated dropwise with **2** ($n = 4$) (2.08 mmol) in 70 mL of EtOH, and stirred for 20.5 h room temperature to yield a yellow precipitate, 164 mg. Chromatography of the filtrate on alumina (C_6H_6) gave 66 mg of a solid, which was combined with the precipitate and chromatographed through alumina (C_6H_6) to yield 190 mg, 38%, of **1** ($n = 4$), orange prisms, mp 197–202 °C dec.[6] Other tropocoronands **1** were obtained as crystals in 25–40% isolated yields from respective aminotropones **3**. The yield for **1** ($n = 2$) was exceptionally low (2%), the main product being 2-phenyl-4,5-dihydroimidazole (**5**).[6] In the case of **3** ($n = 2$)–S–($n = 2$), the *S*-ethylated macrocycle **6**[6] was isolated (6%) in addition to desired **1** ($n = 2$)–S–($n = 2$).

The ^1H NMR, IR, and UV–visible spectra and pK_a values of compounds **1**[12] are very similar to those of the monomeric 1-(methylamino)-7-(methylimino)-1,3,5-cycloheptatriene (**7**),[13] which could also be prepared by the present method. The similarity in data shows that the interaction between the two aminotroponeimine moieties in **1** is minimal.

Addition of ethanolic solutions of M^{2+} salts, M = Fe through Zn, to CH_2Cl_2 solutions of **1** ($n = 3$–6), **1** ($n = 2$)–O–($n = 2$) and **1** ($n = 2$)–S–($n = 2$) led to the development of intense colors indicative of complex formation;[14] several of the new complexes are currently being characterized. The structures of the nickel(II) complexes of **1** ($n = 3$–6) and **1** ($n = 2$)–O–($n = 2$), crystallized from $CHCl_3$–EtOH, have been determined by X-ray diffraction.[15]

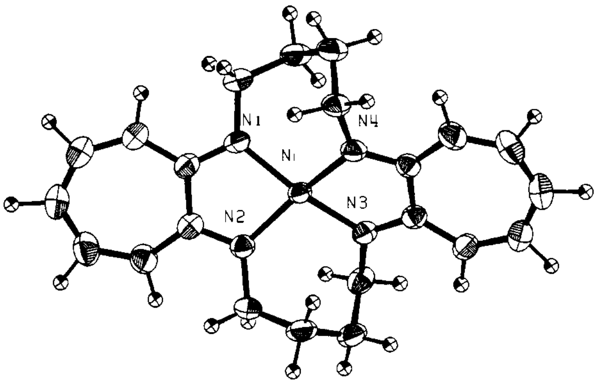


Figure 1. ORTEP diagram of the nickel(II) complex of **1** ($n = 4$) showing the atom labeling scheme and 50% probability thermal ellipsoids. Hydrogen atoms are defined as arbitrary spheres with 1.0-Å radius.

Table II. ^1H NMR Data for Nickel(II) Complexes of Ligands 1[a]

ligands 1 n =	Ar H, deg			methylene H	
	α	β	γ		
3	6.31	6.83	6.16	2.02	2.93
4	6.26	6.76	6.12	1.91	3.35
5	−99.70	60.70	−134.72	12.96	16.05
6	−97.98	61.90	−136.21	0, 17.26, 18.92, 26.40, 244.44, 262.94[b]	

[a] $CDCl_3$, δ from Me_4Si. [b] Assignments of individual methylene groups are not complete.

The geometry of a prototypical member of the series, Ni[**1** ($n = 4$)–H_2], is shown in Figure 1. Selected structural parameters are summarized in Table I.

All five nickel complexes have the metal atoms bonded to the four nitrogen donor atoms of the tropocoronand ligand. As evident from Table I, the dihedral angle θ between the two N–Ni–N planes of the chelating troponeimine rings increases from 8.33° in the **1** ($n = 3$) to 85.2° in the **1** ($n = 6$) derivative. This square planar to pseudotetrahedral transition is a consequence of the constraints brought about by the linking arms of the macrocyclic ligand.[16] This planar/tetrahedral interconversion of the Ni complexes are reminiscent of the earlier studies carried out on Ni(II) complexes of aminotroponeimines[17] and salicylaldimines.[18] In complex **1**

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(9) The absence of HMPA led to the precipitation of a colorless solid, presumably a complex with triethyloxonium tetrafluoroborate: compounds **3** could be converted to imines **4** (Me ethers) by refluxing in toluene with Me_2SO_4 but yields were low, especially for **3** ($n = 2$)–S ($n = 2$).

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(15) X-ray analysis: All structures were solved by standard Patterson, direct methods, and Fourier techniques by using 1209–4590 unique reflections collected out to $2\theta = 50$–55° on a Nonius CAD-4F diffractometer with Mo Kα (λ 0.7107 Å) radiation. Refinement of the data with all atoms assigned anisotropic thermal parameters except hydrogens, which were fixed or refined isotropically with constraints, converged to the values of $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ listed below. The unit cell parameters, space group information, and crystallographic R factors for the nickel(II) complexes of **1** ($n = 3$–6) and **1** ($n = 2$)–O–($n = 2$) are respectively as follows: $a = 10.192$ (2) $b = 8.350$ (1) Å, $c = 10.425$ (1) Å, $\beta = 94.69$ (1)°, $Z = 2$, space group $P2_1$, $R_1 = 0.039$; $a = 11.104$ (1) Å, $b = 8.560$ (2) Å, $c = 20.156$ (2) Å, $\beta = 90.70$ (1)°, $Z = 4$, space group $P2_1/c$, $R_1 = 0.033$; $a = 10.971$ (2) Å, $c = 30.922$ (8) Å, $Z = 6$, space group $P6_122$, $R_1 = 0.050$; $a = 10.682$ (3) Å, $b = 11.396$ (2) Å, $c = 19.331$ (3) Å, $Z = 4$, space group $P2_12_12_1$, $R_1 = 0.042$; $a = 9.397$ (1) Å, $b = 19.913$ (3) Å, $c = 10.718$ (1) Å, $\beta = 95.70$ (6)°, $Z = 4$, space group $P2_1/c$, $R_1 = 0.061$. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported at a later date.

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(n = 3) the low steric demand of the short linking chain permits nickel(II) and its four coordinating nitrogen atoms to adopt the energetically more favorable planar form. As the steric demands of the linker chains increase across the series n = 3 to n = 6, the structure progressively distorts toward the tetrahedral form. This distortion and the accompanying expansion in the Ni-N bond lengths (Table I) are typical for bis-chelate nickel(II) complexes having four nitrogen donor atoms.[17] The present series of complexes provides an interesting demonstration of these structural trends.

The ^{1}H NMR properties of the complexes[12] (Table II) were analogous to those reported for the extensively studied bis(troponeiminato)nickel(II) complexes.[19,20] The molecules formed from ligands **1** (n = 3) and **1** (n = 4) have shifts consistent with their nearly square-planar diamagnetic stereochemistries, whereas the more tetrahedral nickel complexes of **1** (n = 5) and **1** (n = 6) exhibit large isotropic ^{1}H contact shifts owing to the planar ($S = 0$) $\rightleftharpoons$ tetrahedral ($S = 1$) equilibrium.

The tropocoronand ligands thus provide a new class of N_4-coordinating macrocycles, the structures of which can be readily modified. The steric constraints at the metal center can be adjusted to achieve the full range of structures from square planar to tetrahedral; this behavior is illustrated for the complete series of nickel(II) complexes.

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters for the nickel(II) complexes of **1** (n = 3-6) and **1** (n = 2)-O-(n = 2) (5 pages). Ordering information is given on any current masthead page.

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Activation and Transfer of Nitrogen from a Nitridomanganese(V) Porphyrin Complex. The Aza Analogue of Epoxidation

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The discovery that iodosylarenes would transfer oxygen atoms to transition metalloporphyrin complexes to give reactive metal-oxo species[1] and the application of this reaction to the catalytic oxygenation of hydrocarbons[2-4] have suggested that a similar approach could lead to reactive imido or nitrido complexes capable of direct oxidative amination of hydrocarbons. The oxyamination and bis-amination of olefins by imido-osmium complexes has been reported.[5] However, while nitrido complexes of osmium,[6] molybdenum,[7] chromium[8] and manganese[9] and an imido-iron complex[10] are now known, these compounds have not been reported

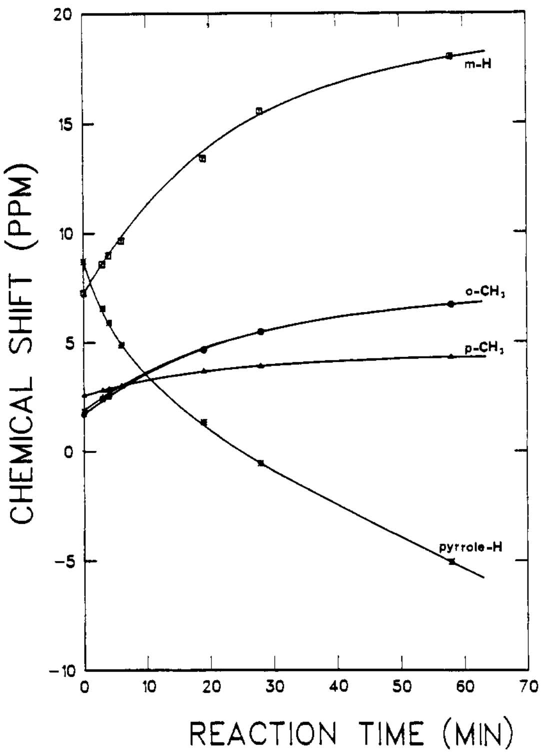

Figure 1. Plots of chemical shifts (δ) vs. reaction time for the reaction of TMPMn(V)N (**1**) with trifluoroacetic anhydride (10 equiv) in methylene chloride at 25 °C.

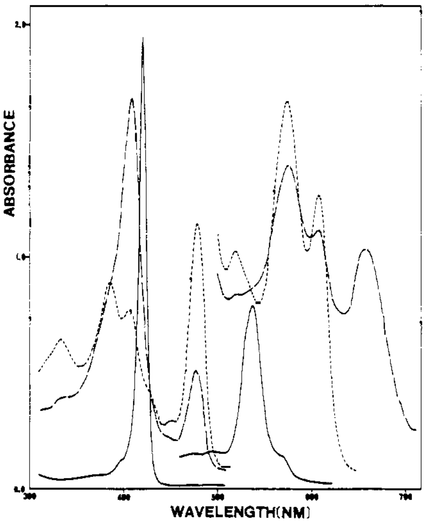

Figure 2. Visible spectra of (a) TMPMn(V)N (3.81×10^{-6} M) in methylene chloride (—) λ_{max} (log ϵ) 420.5 nm (5.71), 5.36 (4.33); (b) TMPMn(V)N (1.52×10^{-5} M) plus 100 equiv of trifluoroacetic anhydride (– –); (c) TMPMnTFA produced after addition of excess cyclooctene to b (- - -).

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