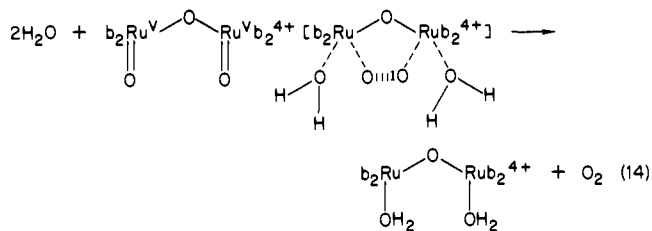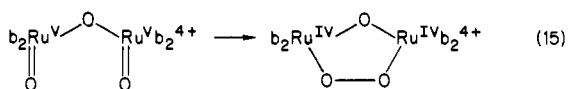or Ru^V). If the oxygen atoms were brought into sufficiently close contact to create an O–O interaction, the net effect could be to trigger the overall transformation to O_2.

$$2H_2O + b_2Ru^V\overset{O}{\diagdown}O\diagup Ru^Vb_2{}^{4+} [b_2Ru\overset{O}{\diagdown}Rub_2{}^{4+}] \longrightarrow$$

$$b_2Ru\overset{O}{\diagdown}Rub_2{}^{4+} + O_2 \quad (14)$$

The coupling process could occur stepwise, perhaps through a peroxo intermediate,

$$b_2Ru^V\overset{O}{\diagdown}Ru^Vb_2{}^{4+} \longrightarrow b_2Ru^{IV}\overset{O}{\diagdown}Ru^{IV}b_2{}^{4+} \quad (15)$$

Another interesting possibility is that for either the IV–V or V–V dimers, the mechanism may involve attack of water on the electron-deficient oxo group, e.g.,

$$b_2Ru^V\overset{O}{\diagdown}Ru^Vb_2{}^{4+} + H_2O \longrightarrow b_2Ru^{III}\overset{O}{\diagdown}Ru^Vb_2{}^{4+} \quad (16)$$
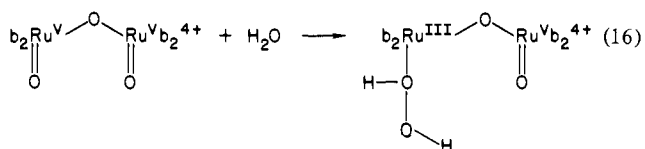
followed by intra- or intermolecular oxidation of bound peroxide or intermolecular oxidation of free H_2O_2. Hopefully, ^{18}O labeling and kinetic studies currently in progress will reveal further details of the mechanism.

With the information concerning redox potentials and reactivity in mind, it is of value to return to the results of the crystallographic study on the Ru^{III}–Ru^{III} dimer. In the structure of the dimer, the 55.7° relative twist angle between the two coordination spheres connected by the oxo group leaves the oxygen atoms of the two coordinated water molecules separated by 4.725 Å, which is well beyond a reasonable O–O interaction distance. Rotation around the Ru–O bond to give a torsoinal angle of 0° would still leave the oxygen atoms of the coordinated water molecules separated by approximately 3.2 Å, as estimated from a molecular model. As a consequence, direct O–O coupling would require a significant distortion of the Ru–O–Ru framework.

Stereochemical and Electronic Spin State Tuning of the Metal Center in the Nickel(II) Tropocoronands

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Abstract: The relationship between the structures and electronic spin states of six nickel(II) complexes of the tropocoronands (TC-n,n'), a new class of metal-complexing macrocycles derived from aminotroponeimines, has been elucidated by single-crystal X-ray diffraction and solid-state magnetic studies. The complexes [Ni(TC-3,3)], [Ni(TC-4,4)], and [Ni(TC-4,5)], having three, four, or a mixture of four and five methylene groups in the two linker chains, are distorted planar molecules with tetrahedral twist angles (θ) of 8.31, 28.9, and 27.1°. Although molecular mechanics calculations reveal [Ni(TC-4,5)] to be sterically strained, the strain energy is not sufficient to convert nickel(II) from the planar, diamagnetic ($S = 0$) electronic state to the pseudotetrahedral, paramagnetic ($S = 1$) form. With five or six atoms in both linker chains the electronic barrier is overcome and distorted tetrahedral structures with $^3T_1$ ground states occur. The resulting complexes [Ni(TC-5,5)], [Ni(TC-2,O,2)], and [Ni(TC-6,6)] have $\theta = 70.1, 74.5$, and 85.2°, respectively. Calculations show the strain energy to derive primarily from bending and torsional constraints in the linker chain backbone. Temperature-dependent magnetic susceptibility studies of solid [Ni(TC-5,5)] and [Ni(TC-6,6)] reveal behavior characteristic of tetrahedral nickel(II) ions with appreciable spin–orbit coupling. The magnetic moments are ~3.1 μ_B at 300 K and ~1.5 μ_B at 8 K. Accompanying the planar-to-tetrahedral transition in the series of nickel(II) tropocoronands is an expansion of the coordination sphere, with average Ni–N bond lengths increasing from 1.861 (7) Å in [Ni(TC-3,3)] to 1.951 (2) Å in [Ni(TC-6,6)]. These results provide a quantitative illustration of how, in a series of closely related nickel(II) complexes, steric constraints in the backbone of the macrocycle combine with the singlet/triplet transition barrier to tune the structural and magnetic properties of the metal center. This information should prove valuable for interpreting the effects of protein-induced constraints on the properties of newly discovered nickel centers in biology.

Tropocoronands are a new class of metal-complexing macrocycles derived from aminotroponeimines (Figure 1). There is substantial interest in the chemistry of transition metal complexes of ligands of this kind, where the size of the metal binding cavity can be controlled by the number of atoms (n) in the linker chains.[2,3]

Moreover, when the two aminotroponeimine poles of the macrocycle become spaced sufficiently far apart the ligand has the potential to become binucleating. The study of binucleating macrocycles is also a topic of considerable current interest.[4]

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Table I. Experimental Details of the X-ray Diffraction Studies

	[Ni(TC-3,3)]	[Ni(TC-4,4)]	[Ni(TC-4,5)]	[Ni(TC-5,5)]	[Ni(TC-2,O,2)]	[Ni(TC-6,6)]
formula	$NiC_{20}H_{22}N_4$	$NiC_{22}H_{26}N_4$	$NiC_{23}H_{28}N_4$	$NiC_{24}H_{30}N_4$	$NiC_{22}H_{26}N_4O_2$	$NiC_{26}H_{34}N_4$
fw	377.13	405.19	419.21	433.24	437.19	461.29
space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P6_122$	$P2_1/c$	$P2_12_12_1$
a, Å	10.192 (2)	11.104 (1)	10.761 (1)	10.971 (2)	9.397 (1)	10.664 (3)
b, Å	8.350 (1)	8.560 (1)	8.962 (1)		19.913 (3)	11.379 (2)
c, Å	10.425 (1)	20.156 (2)	20.455 (2)	30.922 (8)	10.718 (1)	19.295 (3)
β, deg	94.69 (1)	90.70 (1)	90.75 (1)		95.70 (6)	
V, Å^3	884.2	1915.7	1971.5	3223.2	1995.7	2341.4
Z	2	4	4	6	4	4
d_{calcd}, g/cm^3	1.416	1.405	1.412	1.339	1.455	1.308
d_{obsd}, g/cm^3			1.403 (5)^a			
temp, °C	23	24	25	23	24	24
no. of reflctns collected	2033	4574	6399	1773	4978	3074
data collection range, deg	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 55$	$3 \leq 2\theta \leq 55$	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 55$	$3 \leq 2\theta \leq 55$
no. of unique data	1838	4189	4502	1209	4590	3048
no. of obsd data	1566	2934	2639	809	3374	2412
μ(Mo Kα), cm^{-1}	11.07	10.26	9.99	9.19	9.97	8.43
transmission coeff^b	0.86–0.94	0.90–0.92	0.76–0.86	0.87–0.88		0.84–0.91
$R_1{}^c$	0.039	0.033	0.039	0.050	0.061	0.042
$R_2{}^d$	0.051	0.040	0.049	0.059	0.082	0.049
largest shift/esd, final cycle	0.03	0.03	0.01	0.02	0.02	0.003
largest peak, e/Å^3	0.61	0.61	0.55	0.87	0.87	0.60

^{a} By suspension in aqueous CsCl. ^{b} Computed for ψ-scanned reflections with the Wehe–Busing–Levy ORABS program. $^c R_1 = \sum ||F_o| - |F_c||/\sum|F_o|$.
$^d R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.
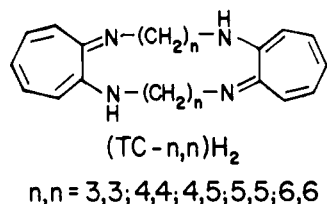

$(TC-n,n)H_2$

$n,n = 3,3; 4,4; 4,5; 5,5; 6,6$

Figure 1. Five of the six tropocoronand ligands used in this work. The protonated forms are depicted. Ligand $H_2(TC-2,O,2)$ has $-CH_2CH_2OCH_2CH_2-$ linker chains.

In order to evaluate the ability of tropocoronand ligands to modulate the structural and electronic properties of transition metal centers, a series of nickel(II) and copper(II) complexes has been studied. In the general case for nickel(II) there is a change in the ground state electronic structure from $S = 0$ to $S = 1$ as the stereochemistry of the complex goes from planar toward tetrahedral. For copper(II), no such difference in spin multiplicities can occur between the planar and tetrahedral limiting geometries.[5] In preliminary work,[6] we learned that the structures of the [Ni(TC-n,n)] complexes distort from planar to tetrahedral across the series from $n = 3$ to 6, but it was not clear whether this distortion was progressive or discontinuous. This point is addressed in the present investigation, which reports synthetic and structural results for [Ni(TC-4,5)] as well as magnetic susceptibility data and X-ray crystallographic details for the complete series of nickel(II) tropocoronands. Subsequent papers describe related mononuclear and, for large n, binuclear copper(II) complexes.[7] The ligand syntheses and NMR spectral properties of the nickel(II) compounds are reported elsewhere.[8]

Experimental Section and Results

The syntheses of the tropocoronands and most of the nickel(II) complexes may be found in ref 8. Nickel(II) acetate dihydrate (Baker) was used without further purification. Electronic spectra were measured in methylene chloride solutions on a Cary 118C spectrophotometer. Infrared spectra were taken on samples pelleted with KBr and recorded on

Table II. Final Positional Parameters for Ni(TC-3,3)^a

Atom	x	y	z
Ni1	-0.31681(7)	-0.2500	-0.33651(6)
N1	-0.3513(5)	-0.1300(7)	-0.1935(5)
N2	-0.1706(5)	-0.1348(7)	-0.3821(5)
N3	-0.2944(5)	-0.3530(6)	-0.4920(5)
N4	-0.4714(5)	-0.3530(7)	-0.3025(5)
C1	-0.2626(7)	-0.0156(10)	-0.1272(6)
C2	-0.1231(7)	-0.0460(11)	-0.1581(6)
C3	-0.0927(8)	-0.0238(10)	-0.2977(6)
C4	-0.5210(7)	-0.4998(9)	-0.3645(7)
C5	-0.4121(8)	-0.5898(8)	-0.4252(7)
C6	-0.3641(7)	-0.4985(9)	-0.5359(7)
C11	-0.4740(7)	-0.1453(8)	-0.1537(5)
C12	-0.5189(8)	-0.0468(10)	-0.0588(6)
C13	-0.6413(8)	-0.0442(10)	-0.0072(6)
C14	-0.7555(8)	-0.1310(11)	-0.0401(7)
C15	-0.7680(6)	-0.2481(14)	-0.1323(6)
C16	-0.6802(7)	-0.3151(9)	-0.2098(6)
C17	-0.5468(6)	-0.2756(9)	-0.2221(5)
C21	-0.1429(6)	-0.1448(8)	-0.5033(6)
C22	-0.0443(7)	-0.0538(9)	-0.5576(7)
C23	-0.0045(7)	-0.0473(10)	-0.6822(8)
C24	-0.0529(7)	-0.1285(11)	-0.7915(7)
C25	-0.1501(7)	-0.2454(15)	-0.7972(6)
C26	-0.2192(7)	-0.3107(9)	-0.7030(6)
C27	-0.2199(6)	-0.2757(9)	-0.5707(6)

^{a} Numbers in parentheses are errors in the last significant digit(s).

a Beckman Acculab 10 instrument calibrated with polystyrene film.

Synthesis of [Ni(TC-4,5)]. To a solution of 25 mg (0.069 mmol) of $H_2(TC-4,5)$ in 10 mL of CH_2Cl_2 was added 15 mg of $Ni(O_2CCH_3)_2 \cdot 2H_2O$ in 3 mL of ethanol. The yellow solution of the tropocoronand turned deep red-brown upon addition of the metal salt. The solution was evaporated on a steam bath to leave a red-brown solid which was recrystallized from $CH_2Cl_2/EtOH$ to yield 23 mg (80%) of [Ni(TC-4,5)]. Anal. Calcd for $C_{23}H_{28}N_4Ni$: C, 65.90; H, 6.73; N, 13.36. Found: C, 66.51; H, 7.23; N, 12.46. Electronic spectra, λ_{max} (nm) (ϵ, M^{-1} cm^{-1}): 751 (825), 442 (15 700), 370 (17 200). Infrared 2920 (w), 2850 (w), 1585 (s), 1500 (s), 1445 (m), 1430 (s), 1400 (s), 1285 (s), 1225 (s), 1015 (m), 730 (s) cm^{-1}.

X-ray Structural Work. Table I summarizes the details of data collection, reduction, and refinement; typical procedures in our laboratory are further described in ref 9. All data were collected on an Enraf–Nonius CAD4F diffractometer with monochromatized Mo Kα (λ 0.7107 Å) radiation and $\theta/2\theta$ scans.

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(9) Silverman, L. D.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

Table III. Final Positional Parameters for Ni(TC-4,4)[a]

Atom	x	y	z
N1	0.13937(3)	0.22446(4)	0.19852(2)
N11	0.20607(19)	0.1642(3)	0.28001(10)
N12	0.28521(19)	0.3326(3)	0.19317(10)
N21	-0.0264(2)	0.1835(3)	0.21270(10)
N22	0.0905(2)	0.2230(3)	0.10802(10)
C11	-0.0278(3)	0.2078(3)	0.09731(13)
C12	-0.0824(3)	0.2335(4)	0.03470(15)
C13	-0.2013(3)	0.2201(5)	0.01327(17)
C14	-0.3018(3)	0.1691(5)	0.04594(18)
C15	-0.3058(3)	0.1218(4)	0.11181(17)
C16	-0.2160(3)	0.1220(4)	0.15946(15)
C17	-0.0943(3)	0.1712(3)	0.15840(13)
C1	-0.0907(3)	0.1805(4)	0.27672(13)
C2	-0.0225(3)	0.2582(4)	0.33346(14)
C3	0.0608(3)	0.1467(4)	0.37155(13)
C4	0.1421(3)	0.0576(3)	0.32411(13)
C21	0.3121(3)	0.2231(3)	0.29749(12)
C22	0.3667(3)	0.1985(3)	0.36050(14)
C23	0.4770(3)	0.2467(3)	0.38618(15)
C24	0.5671(3)	0.3322(4)	0.35726(17)
C25	0.5662(3)	0.3935(4)	0.29380(18)
C26	0.4781(3)	0.3869(4)	0.24425(16)
C27	0.3630(2)	0.3188(3)	0.24349(13)
C1A	0.3094(3)	0.4364(3)	0.13728(13)
C2A	0.3706(3)	0.3494(4)	0.08074(15)
C3A	0.3000(3)	0.2031(4)	0.06186(15)
C4A	0.1672(3)	0.2320(4)	0.04825(14)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table IV. Final Positional Parameters for Ni(TC-4,5)[a]

Atom	x	y	z
N1	0.14016(4)	0.12282(5)	0.19521(2)
N1	0.0872(2)	0.1255(3)	0.10500(12)
N2	-0.0281(2)	0.1753(3)	0.20897(12)
N3	0.2950(2)	0.0257(3)	0.19368(12)
N4	0.2045(2)	0.1909(3)	0.27476(11)
C11	-0.0163(3)	0.2073(4)	0.09621(14)
C12	-0.0475(3)	0.2812(4)	0.03749(15)
C13	-0.1562(4)	0.3464(4)	0.01572(18)
C14	-0.2706(4)	0.3533(5)	0.04464(19)
C15	-0.2968(3)	0.3048(4)	0.10631(18)
C16	-0.2210(3)	0.2471(4)	0.15460(17)
C17	-0.0918(3)	0.2154(3)	0.15548(15)
C21	0.3703(3)	0.0429(3)	0.24504(15)
C22	0.4901(3)	-0.0220(4)	0.25103(18)
C23	0.5749(3)	-0.0255(4)	0.30186(18)
C24	0.5710(3)	0.0385(4)	0.36320(19)
C25	0.4766(3)	0.1257(4)	0.38666(17)
C26	0.3661(3)	0.1699(4)	0.35739(16)
C27	0.3134(3)	0.1391(3)	0.29555(14)
C1A	-0.1007(3)	0.1578(4)	0.26994(16)
C2A	-0.0280(3)	0.0950(4)	0.32705(17)
C3A	0.0513(3)	0.2082(5)	0.36305(15)
C4A	0.1341(3)	0.2954(4)	0.31574(15)
C1B	0.1485(3)	0.0763(4)	0.04414(16)
C2B	0.2623(3)	0.1619(5)	0.02389(16)
C3B	0.3735(3)	0.1578(4)	0.07020(16)
C4B	0.4153(3)	0.0015(4)	0.08981(17)
C5B	0.3334(3)	-0.0740(4)	0.14063(15)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table V. Final Positional Parameters for Ni(TC-5,5)[a]

Atom	x	y	z
N1	-0.41655(8)	-0.83310(15)	-0.2500
N1	-0.4513(7)	-0.6777(7)	-0.25971(19)
N2	-0.4299(7)	-0.9884(7)	-0.28438(19)
C11	-0.3413(8)	-0.5506(9)	-0.2575(2)
C12	-0.3419(9)	-0.4269(9)	-0.2701(2)
C13	-0.2413(11)	-0.2854(10)	-0.2677(3)
C14	-0.1112(7)	-0.2225(13)	-0.2500
C21	-0.5253(8)	-1.1169(9)	-0.2713(2)
C22	-0.5667(9)	-1.2372(10)	-0.2964(3)
C23	-0.6537(10)	-1.3794(10)	-0.2871(3)
C24	-0.7209(6)	-1.4418(12)	-0.2500
C1	-0.5898(10)	-0.6957(10)	-0.2706(3)
C2	-0.7141(9)	-0.8358(10)	-0.2551(4)
C3	-0.3513(10)	-0.9684(9)	-0.3243(3)
C4	-0.2036(12)	-0.8400(10)	-0.3221(3)
C5	-0.0999(10)	-0.8436(10)	-0.2910(4)

[a] Numbers in parentheses are errors in the last significant digit(s).

[Ni(TC-3,3)]. A small black crystal of dimensions 0.06 × 0.14 × 0.35 mm was found to be monoclinic by preliminary study on the Weissenberg camera and diffractometer. The space group was determined to be $P2_1$ (C_2^2, No. 4)[10] from the systematic absences and, ultimately, the solution and successful refinement of the structure. The unit cell parameters were refined by using the setting angles of 25 reflections having $2\theta \geqslant 25°$. Standard reflections showed no crystal decay. No absorption correction was made. The structure was solved by standard Patterson and difference Fourier techniques and refined with anisotropic temperature factors for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The correctness of the enantiomeric description for the polar space group was confirmed by comparison of agreement factors for the two possible choices. The function minimized was $\sum w(|F_o| - |F_o|)^2$, where $w = 1.4136/[\sigma^2(F_o) + 0.000625F_o^2]$. Calculations were carried out with the program package SHELX-76[11] on a DEC VAX-11/780 computer. Atomic scattering factors for the neutral atoms and anomalous dispersion corrections were taken from ref 12. Final coordinates for the non-hydrogen atoms are given in Table II. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, all bond lengths and angles, and observed and calculated structure factors are available as supplementary material (Tables S1–S4).

[Ni(TC-4,4)]. A crystal of dimensions 0.08 × 0.10 × 0.50 mm was studied on the diffractometer. The space group was determined to be $P2_1/c$ (C_{2h}^5, No. 14) from the systematic absences.[10] A 6% decrease in the intensities of the standard reflections during data collection was corrected and the structure solved and refined as described above for [Ni(TC-3,3)]. The weighting scheme employed set $w = 0.7268/[\sigma^2(F_o) + 0.000625F_o^2]$. Other details are as described above for [Ni(TC-3,3)]. Atomic coordinates are given in Table III. Anisotropic thermal parameters, hydrogen positional and thermal parameters, bond distances and angles, and structure factors appear as Tables S5–S8, respectively.

[Ni(TC-4,5)]. The data crystal was a red-brown needle bounded by (001) and (00Ī), 0.075 mm apart, (010) and (0Ī0), 0.49 mm apart, and (100) and (Ī00), 0.13 mm apart. The systematic absences were consistent with space group $P2_1/c$ (C_{2h}^5, No. 14).[10] The structure was solved and refined as described above, with hydrogen atoms placed at fixed C–H distances of 0.95 Å and constrained to ride on the respective carbon

(10) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I.

(11) Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R.; van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 34.

(12) (a) Non-hydrogen atoms: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99 and 149. (b) Hydrogen atoms: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

atoms. Groups of similar (aliphatic or aromatic) hydrogen atoms were given common isotropic thermal parameters. Weights were assigned as $w = 0.9939/[\sigma^2(F_o) + 0.000625F_o^2]$. The final positional parameters for the non-hydrogen atoms may be found in Table IV. Tables S9–S12 summarize respectively anisotropic thermal parameters, hydrogen atom parameters, interatomic distances and angles, and structure factors.

[Ni(TC-5,5)]. By using a crystal of dimensions 0.08 × 0.10 × 0.17 mm, the hexagonal unit cell parameters were determined by diffractometry and confirmed by study on the Weissenberg camera. The systematic absence 000*l*, $l \neq 6n$, indicated the space group to be $P6_122$ (D_6^2, No. 178) or its enantiomorph $P6_522$ (D_6^3, No. 179).[10] Data were collected and the structure was solved in $P6_522$ by direct methods with MULTAN-78[13] and difference Fourier maps. Aliphatic hydrogen atoms were located on these maps after the aminotroponeimine ring protons were placed in their calculated positions. Aliphatic protons were assigned a temperature factor of $U = 0.06$ Å^2, an overall isotropic temperature factor for the ring protons was refined, and all non-hydrogen atoms were given anisotropic thermal parameters. Toward the end of the refinement, in which the weights were set as $w = 1.8278[\sigma^2(F_o) + 0.000625F_o^2]$, the absolute configuration was checked by inverting the coordinates through the origin and refining in space group $P6_122$. This latter choice proved to be correct, as judged by a reduction in R_2 from 0.056 to 0.050. Final non-hydrogen atomic coordinates are reported in Table V. Anisotropic thermal parameters, interatomic distances and angles, final hydrogen atom positions and thermal parameters, and structure factors may be found in Tables S13–S16, respectively.

[Ni(TC-2,O,2)]. By using a small crystal of dimensions 0.10 × 0.12 × 0.12 mm the unit cell and space group $P2_1/c$ (C_{2h}^5, No. 14)[10] were determined, and intensity data were collected on the diffractometer. The

Nickel(II) Tropocoronands

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Table VI. Final Positional Parameters for Ni(TC-2,O,2)[a]

Atom	x	y	z
N1	0.11247(6)	0.09683(3)	0.24810(5)
O1	-0.0370(4)	0.25417(18)	0.1627(3)
O2	0.2572(4)	-0.05213(16)	0.3436(3)
N11	0.0340(4)	0.01498(17)	0.1729(3)
N12	0.9092(4)	0.11590(19)	0.2490(3)
N21	0.2322(4)	0.17133(17)	0.2089(3)
N22	0.2600(4)	0.09076(18)	0.3918(3)
C11	0.8920(4)	0.0055(2)	0.1719(4)
C12	0.8242(5)	-0.0535(2)	0.1293(5)
C13	0.6810(6)	-0.0727(3)	0.1196(6)
C14	0.5620(6)	-0.0391(3)	0.1501(7)
C15	0.5611(5)	0.0246(3)	0.2006(6)
C16	0.6707(5)	0.0700(3)	0.2294(5)
C17	0.8203(5)	0.0659(2)	0.2174(4)
C18	-0.1496(5)	0.1798(2)	0.2954(5)
C19	-0.0460(5)	0.2360(2)	0.2911(5)
C110	0.1000(5)	0.2751(2)	0.1335(5)
C111	0.1928(5)	0.2161(2)	0.1015(4)
C21	0.3378(4)	0.1883(2)	0.2946(4)
C22	0.4186(5)	0.2475(3)	0.2869(5)
C23	0.5330(5)	0.2751(3)	0.3641(5)
C24	0.6042(5)	0.2496(3)	0.4730(5)
C25	0.5747(5)	0.1902(3)	0.5290(5)
C26	0.4687(5)	0.1436(3)	0.4997(4)
C27	0.3565(4)	0.1393(2)	0.4003(4)
C28	0.2666(6)	0.0384(3)	0.4867(5)
C29	0.1833(6)	-0.0231(3)	0.4400(5)
C210	0.1691(5)	-0.0860(2)	0.2491(5)
C211	0.1268(5)	-0.0395(2)	0.1390(4)

[a] Numbers in parentheses are errors in the last significant digit(s).

structure was solved by direct methods[13] and refined as described above for [Ni(TC-5,5)]. Weights were defined as $w = 1.5498/[\sigma^2(F_o) + 0.000625F_o^2]$. Final positional parameters are given in Table VI, while Tables S17–S20 contain final anisotropic thermal parameters, hydrogen atom coordinates and temperature factors, interatomic distances and angles, and observed and calculated structure factors, respectively.

[Ni(TC-6,6)]. A crystal of dimensions 0.15 × 0.15 × 0.53 mm was found by diffractometry to belong to the orthorhombic crystal class, space group $P2_12_12_1$. The structure was solved and refined as described for [Ni(TC-4,5)], with weights defined as $w = 0.9382/[\sigma^2(F_o) + 0.000625F_o^2]$. Positional parameters for the non-hydrogen atoms are given in Table VI. Summarized in Tables S21–S24 are respectively the anisotropic temperature factors, hydrogen atom coordinates and thermal parameters, bond lengths and angles, and a listing of observed and calculated structure factors.

Magnetic Susceptibility Measurements. Magnetic data were taken on 6–13 mg solid samples of the nickel(II) tropocoronands. Samples were loaded into Al–Si alloy buckets and measured with an S.H.E. Corp. Model 905 SQUID-type susceptometer operating at 25 kG over the range $8 \leq T \leq 300$ K. Molar susceptibilities for each complex were calculated following corrections for bucket paramagnetism and underlying atomic diamagnetism.[14] The constitutive effect of the tropocoronand ligand was extrapolated from the measured susceptibility, -253×10^{-6} cgs/mol, of H_2(TC-6,6). The high-temperature ($T > 80$ K) corrected molar susceptibilities for [Ni(TC-5,5)] and [Ni(TC-6,6)] were fit to the Curie–Weiss law, eq 1, by the method of least squares in which the variable

$$\chi_M = C/(T - \theta) + N\alpha \qquad (1)$$

parameters were C, the Curie constant, θ, the Weiss constant, and $N\alpha$, the temperature-independent paramagnetism. Further information about the methods used by us to obtain magnetic susceptibility data may be found in ref 15.

The three complexes [Ni(TC-3,3)], [Ni(TC-4,4)], and [Ni(TC-4,5)] are all diamagnetic in the solid state. Corrected molar magnetic susceptibilities measured below 20 K for these complexes are summarized in Table S25. On the other hand, [Ni(TC-5,5)] and [Ni(TC-6,6)] are paramagnetic. Above 80 K they obey the Curie–Weiss law with effective

(13) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M.: MULTAN-78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.

(14) Sellwood, P. W. "Magnetochemistry", 2nd ed.; Interscience: New York, 1965; p 693.

(15) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. C.; Lippard, S. J. J. Am. Chem. Soc. 1984, 106, 3653.
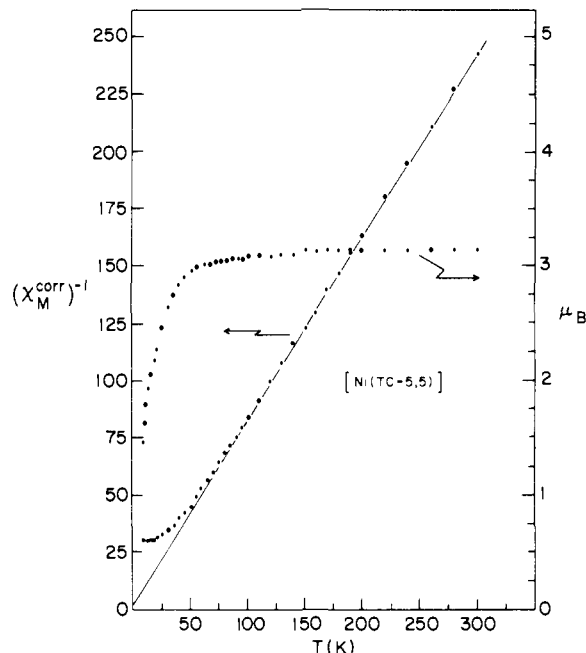
Figure 2. Plots of corrected molar susceptibility and effective magnetic moment for [Ni(TC-5,5)] as a function of temperature. The solid line was calculated for the high-temperature data by the Curie–Weiss law as described in the text.

Table VII. Final Positional Parameters for Ni(TC-6,6)[a]

Atom	x	y	z
N1	0.15770(5)	0.09931(4)	0.36771(3)
N11	0.1593(4)	0.2397(3)	0.42507(18)
N12	0.3201(3)	0.1629(3)	0.34087(19)
N21	0.0099(3)	0.0557(3)	0.31428(19)
N22	0.1304(3)	-0.0589(3)	0.40345(18)
C11	0.0301(4)	-0.1140(3)	0.38207(19)
C12	-0.0058(5)	-0.2271(4)	0.4069(2)
C13	-0.1124(5)	-0.2950(4)	0.3963(3)
C14	-0.2127(5)	-0.2769(4)	0.3533(3)
C15	-0.2281(5)	-0.1838(4)	0.3075(3)
C16	-0.1532(4)	-0.0869(4)	0.2963(2)
C17	-0.0426(4)	-0.0464(4)	0.3291(2)
C18	-0.0451(5)	0.1354(4)	0.2616(3)
C19	-0.1656(5)	0.1988(4)	0.2843(3)
C110	-0.1611(5)	0.2464(4)	0.3581(3)
C111	-0.0704(5)	0.3489(4)	0.3665(3)
C112	-0.0292(5)	0.3687(5)	0.4418(3)
C113	0.0541(5)	0.2694(4)	0.4704(2)
C21	0.2592(4)	0.3081(4)	0.4202(2)
C22	0.2737(5)	0.4110(4)	0.4615(3)
C23	0.3658(6)	0.4969(5)	0.4629(3)
C24	0.4739(6)	0.5080(5)	0.4223(3)
C25	0.5137(5)	0.4316(5)	0.3726(3)
C26	0.4638(5)	0.3266(4)	0.3508(3)
C27	0.3534(4)	0.2650(3)	0.3686(2)
C28	0.4015(4)	0.1028(5)	0.2908(2)
C29	0.5123(5)	0.0367(5)	0.3237(3)
C210	0.4747(5)	-0.0466(5)	0.3810(3)
C211	0.3859(5)	-0.1447(4)	0.3581(3)
C212	0.3109(5)	-0.1987(4)	0.4173(3)
C213	0.2190(5)	-0.1128(4)	0.4520(2)

[a] Numbers in parentheses are errors in the last significant digit(s).

magnetic moments of 3.18 ± 0.01 and 3.11 ± 0.01 μ_B, respectively. At lower temperatures, the moments decrease, becoming 1.46 μ_B for [Ni(TC-5,5)] and 1.56 μ_B for [Ni(TC-6,6)] at 8 K. A complete listing of observed molar magnetic susceptibilities and magnetic moments for these two complexes is available in Tables S26 and S27, respectively. Plots of χ_M^{-1} and μ_{eff} vs. temperature are displayed in Figures 2 and 3.

Discussion

The Stereochemistry of Nickel(II) Tropocoronands. All six nickel(II) tropocoronands studied here crystallize as discrete
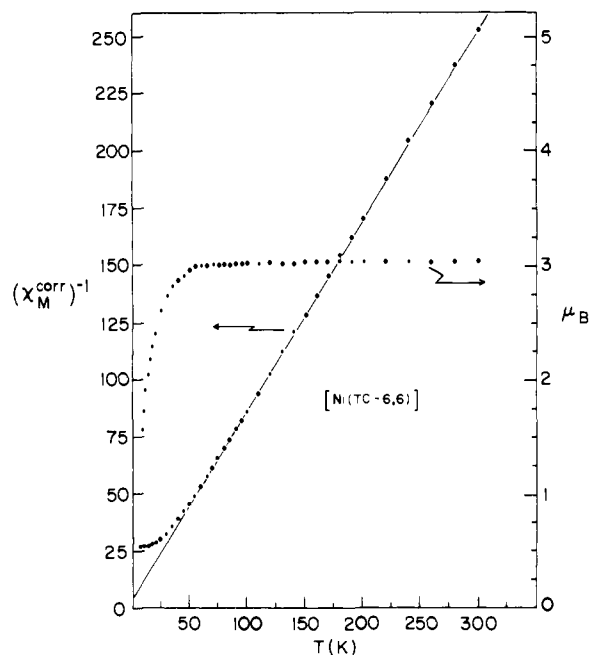
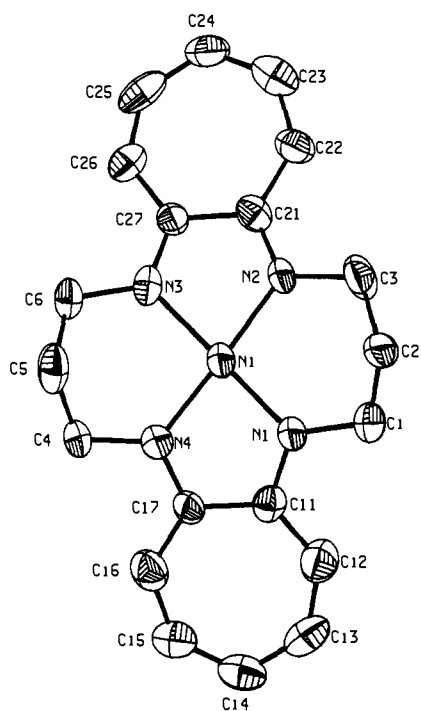**Figure 3.** Magnetic data for [Ni(TC-6,6)] plotted as described in the caption to Figure 2.

Figure 4. Structure of [Ni(TC-3,3)].

Figure 5. Structure of [Ni(TC-4,4)].

Figure 6. Structure of [Ni(TC-4,5)].

mononuclear four-coordinate complexes (Figures 4–9). A summary of selected bond lengths and interbond angles for these complexes is given in Table VIII. As the number of atoms in the linker chains increases, the geometry at nickel distorts from planar toward tetrahedral. This distortion is measured by the dihedral angle θ between the two sets of planes defined by the nickel and two nitrogen atoms of the troponeiminate 5-membered chelate rings. From the θ values in Table VIII it is apparent that the planar-to-tetrahedral transition is discontinuous. The complexes [Ni(TC-3,3)], [Ni(TC-4,4)], and [Ni(TC-4,5)] are distorted planar molecules, $8.33° \leqslant \theta \leqslant 28.9°$, whereas [Ni(TC-5,5)], [Ni(TC-2,0,2)], and [Ni(TC-6,6)] are distorted tetrahedra, $70.1° \leqslant \theta \leqslant 85.2°$. The steric factors, described below, that tend to distort the nickel center toward a tetrahedral geometry are counterbalanced by another force which is only overcome, in a
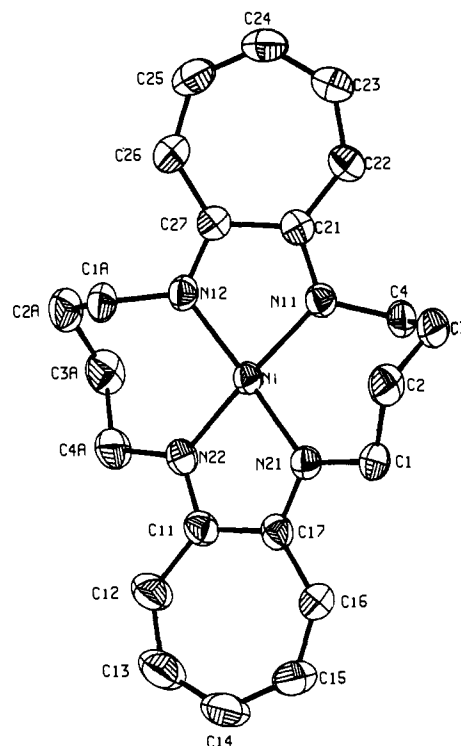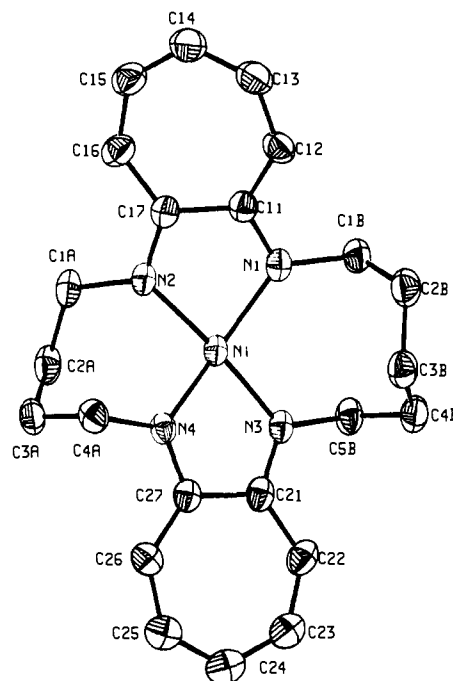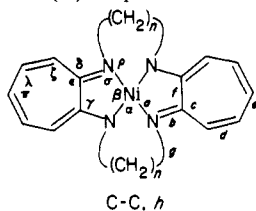
stepwise manner, at [Ni(TC-5,5)]. This opposing force is the change in spin state from the more favored planar, singlet ($S = 0$) to the energetically higher lying tetrahedral, triplet ($S = 1$) form. As revealed by the susceptibility measurements, the magnetic transition also occurs between [Ni(TC-4,5)] and [Ni(TC-5,5)]. Thus 30° appears to be the critical value for the distortion parameter θ that gives rise to the change in spin state. These results are consistent with previous studies of four-coordinate nickel(II) complexes,[5,16] although the present series of nickel(II) tropocoronands constitutes an especially clear manifestation of this phenomenon. In the related copper(II) tropocoronands, where

(16) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1976; p 789.

Table VIII. Summary of Structural Information for the Nickel(II) Tropocoronands[a]

	[Ni(TC-3,3)]	[Ni(TC-4,4)]	[Ni(TC-4,5)]	[Ni(TC-5,5)]	[Ni(TC-2,O,2)]	[Ni(TC-6,6)]
θ^b	8.33	28.9	27.1	70.1	74.5	85.2
a	1.861 (7)	1.883 (4)	1.891 (22)[c]	1.949 (2)	1.946 (16)	1.951 (2)
b	1.34 (2)	1.329 (4)	1.332 (7)	1.323 (10)	1.330 (10)	1.322 (8)
c	1.41 (1)	1.412 (5)	1.413 (6)	1.41 (1)	1.413 (14)	1.422 (5)
d	1.38 (1)	1.386 (6)	1.377 (4)	1.39 (0)	1.388 (11)	1.384 (6)
e	1.38 (1)	1.381 (6)	1.373 (5)	1.35 (0)	1.375 (6)	1.383 (15)
f	1.48 (1)	1.479 (2)	1.477 (7)	1.51 (1)	1.488 (5)	1.499 (1)
g	1.459 (5)	1.474 (11)	1.478 (8)	1.465 (5)	1.470 (14)	1.473 (8)
h	1.513 (9)	1.524 (5)	1.519 (11)	1.51 (3)	1.511 (15)[d]	1.533 (9)
σ	115.9 (5)	116.7 (2)	115.9 (2.7)	116.1 (3)	116.6 (6)	116.95 (11)
α	97.3 (5)	101.1 (4)	104.0 (1) 97.7 (1)	115.4 (0)	117.7 (1.4)	121.6 (3)
ρ	125.2 (5)	124.5 (3.5)[c]	126.1 (4.2)	123.7 (4)	123.0 (1.5)	121.6 (3)
β	82.4 (5)	82.2 (7)	81.8 (6)	81.6 (2)	80.6 (2)	80.5 (2)
γ	111.3 (4)	112.0 (8)	111.7 (8)	112.9 (2)	112.7 (8)	112.6 (5)
δ	123.2 (9)	123.2 (4)	124.2 (2)	123.5 (7)	122.8 (2)	123.0 (7)
ϵ	125.4 (9)	124.8 (5)	124.1 (7)	123.5 (5)	124.4 (8)	124.3 (4)
ζ	130.6 (1.0)	131.5 (5)	131.7 (4)	132.2 (9)	132.1 (6)	132.3 (3)
λ	131.0 (1.0)	130.1 (5)	130.5 (4)	130 (0)	130.5 (7)	130.0 (4)
π	125.4 (4)	126.3 (4)	125.6 (2)	128 (0)	125.7 (2)	126.4 (1)

[a] Bond lengths are in Å and interbond angles are in degrees. Standard deviations are computed as $[(\sum x^2 - n\bar{x}^2)/n]^{1/2}$. [b] Dihedral angle between NiN_2 planes as defined in the text. [c] Mean value of two disparate sets. [d] The C–O mean distance is 1.422 (7) Å.
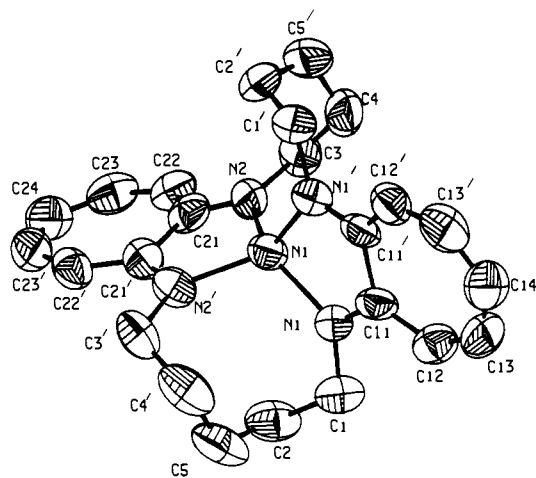

Figure 7. Structure of [Ni(TC-5,5)]. Primed and unprimed atoms are related by a crystallographically required C_2 symmetry axis.

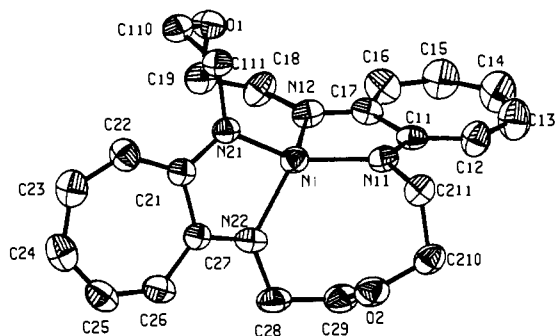**Figure 8.** Structure of [Ni(TC-2,O,2)].

Figure 9. Structure of [Ni(TC-6,6)].

the planar and tetrahedral limiting geometric forms cannot differ in spin state, the distortion is progressive as expected.[5,7]

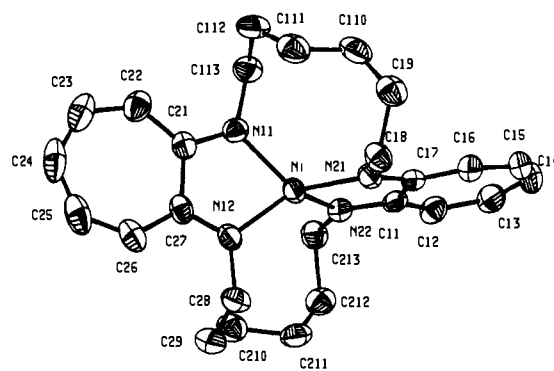Table VIII further reveals that the planar-to-tetrahedral distortion is accompanied by other geometric alterations in structure besides the increase in θ. In particular, the average Ni–N bond lengths increase from 1.86 to 1.95 Å and the N–Ni–N angle (α) in the saturated chelate ring opens from 97 to 122°. Both changes occur mainly between [Ni(TC-4,5)] and [Ni(TC-5,5)]. These structural modifications result from the steric strain imposed by packing an increasing number of methylene groups between the two saturated carbon atoms bonded to the nitrogen atoms of the troponeiminate groups. Molecular mechanics calculations[17,18] were carried out to pinpoint the source of this steric strain. In [Ni-(TC-3,3)], the complex nearest to the square-planar limit, these saturated end-carbon atoms are 2.54 Å apart. In the MM-2 calculations, the end (α,ω) carbon atoms of a series of saturated linear alkanes, C_nH_{2n+2}, n = 3–6, and the related ether, $(C_2H_5)_2O$, were fixed at a distance of 2.54 Å and energy minization was performed. The results of these computations were then compared with identical ones carried out with the experimentally observed C_α–C_ω distances, 2.95 Å for [Ni(TC-4,4)], 2.95 and 3.09 Å for [Ni(TC-4,5)], 4.09 Å for [Ni(TC-5,5)], 4.10 Å for [Ni(TC-2,-

(17) Molecular mechanics calculations were performed on a VAX 11-780 computer with the program MODELA by W. C. Still of Columbia University as modified by R. M. Hanson of M.I.T. This program employs MM-2, a conformational analysis program by Allinger.[18]

(18) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

O,2)], and 4.44 Å for [Ni(TC-6,6)]. In all cases the shorter fixed end point molecules were energetically less favored, with the bending and torsional contributions being the most severe.[18] In a model calculation for [Ni(TC-6,6)] the end points were further relaxed to a distance of 6.9 Å, revealing additional release of strain energy. This result demonstrates that even the observed tetrahedral structure of [Ni(TC-6,6)] is sterically constrained, and it provides a rationale for the propensity of copper(II) to form a binuclear complex with this ligand.[7]

Other features of the geometry of the nickel(II) tropocoronands are summarized in Table VIII. The troponeiminate rings are all essentially planar, with the nickel atom lying within ±0.4 Å of the mean ligand planes. The bite angle in the 5-membered ring, β, is nearly constant across the series, ~82°.

Magnetic Properties. The effective magnetic moments of the solid nickel(II) tropocoronands exhibit the same step function dependence on the number of linker chain atoms as do the molecular geometries. Square-planar complexes displaying maximal tetrahedral distortion, $\theta < 30°$, are all diamagnetic (S = 0) whereas the pseudotetrahedral complexes, $\theta > 70°$, have effective magnetic moments consistent with $S = 1$ spin states. The temperature dependence of the magnetic moments of [Ni(TC-5,5)] and [Ni(TC-6,6)] is typical of pseudotetrahedral nickel(II) complexes having $^3T_1$ ground terms.[19] Spin–orbit coupling splits the ground term into three levels having $J = 0, 1$, and 2. Analysis[20] of the powder and single crystal magnetic susceptibility data for the related complex, bis(N-isopropylsalicylideneiminato)nickel(II), having $\theta = 81.5°$,[21] using the angular overlap model, gave good agreement between observed and theoretically calculated moments. This complex has an effective moment of 2.25 μ_B at 20 K and 3.23 μ_B at 295 K, close to the values we find for [Ni(TC-5,5)] and [Ni(TC-6,6)]. To fit our observed magnetic susceptibility data to the theoretical expression for χ vs. T would require knowledge of parameters best obtained from single-crystal magnetic anisotropy measurements.[20] The information obtained from such fits would not alter the basic conclusions of this work, however. NMR studies[8] of the nickel(II) tropocoronands in solution reveal diamagnetic behavior for [Ni(TC-3,3)] and [Ni(TC-4,4)], even at elevated temperatures, and isotropically shifted spectra for the paramagnetic [Ni(TC-5,5)], [Ni(TC-2,-O,2)], and [Ni(TC-6,6)] complexes. The position of the planar (S = 0) ⇌ tetrahedral (S = 1) equilibrium shifts with temperature for these last three compounds, which have the same magnetic properties in both the solid state and solution. The existence of this equilibrium in solution was further established when a single crystal of the chiral [Ni(TC-5,5)] complex (space group $P6_122$, Table I) failed to show optical activity by circular dichroism measurements.[8]

Summary and Overview. Steric forces resulting from the angle bending and torsional strain that occur when an increasing number of methylene and/or ether links is added to the chain connecting the two poles of the tropocoronand macrocycles distort the geometry at nickel(II) from planar (S = 0) to tetrahedral (S = 1). Because of the opposing electronic force which favors the spin singlet form, the transition is discontinuous. The discontinuity occurs between [Ni(TC-4,5)], $\theta = 27.1°$, and [Ni(TC-5,5)], $\theta = 70.1°$. These results nicely complement those recently reported for nickel(II) corphinoid complexes in which the NiN$_4$ coordination sphere is much more rigid and steric constraints are manifest by ruffling at the ligand periphery.[22] Information gained from studies of a series of related molecules in which the ligand steric forces tune the electronic properties of the metal center, and vice versa, will be valuable as more is learned about the occurrence and functions of nickel in biology.[23]

Registry No. Ni(Tc-3,3), 84927-32-2; Ni(Tc-4,4), 84927-33-3; Ni-(Tc-4,5), 96412-26-9; Ni(Tc-5,5), 84959-54-6; Ni(Tc-2,0,2), 96412-27-0; Ni(Tc-6,6), 84943-95-3.

Supplementary Material Available: Tables S1–S27 reporting heavy-atom thermal parameters, hydrogen atom positional and thermal parameters, bond lengths and angles, and observed and calculated structure factors for the six nickel(II) tropocoronand structures as well as magnetic susceptibility data (82 pages). Ordering information is given on any current masthead page.

(19) Figgis, B. N. "Introduction to Ligand Fields"; Interscience: New York, 1966; p 273.

(20) Cruse, D. A.; Gerloch, M. *J. Chem. Soc., Dalton Trans.* **1977**, *152.*

(21) Fox, M. R.; Orioli, P. L.; Lingafelter, E. C.; Sacconi, L. *Acta Crystallogr.* **1964**, *17*, 1159.

(22) (a) Fässler, A.; Pfaltz, A.; Kräutler, B.; Eschenmoser, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1365. (b) Kratky, C.; Fässler, A.; Pfaltz, A.; Kräutler, B.; Jaun, B.; Eschenmoser, A. *Ibid.* **1984**, 1368.

(23) (a) Hausinger, R. P.; Orme-Johnson, W. H.; Walsh, C. *Biochemistry* **1984**, *23*, 801. (b) Livingston, D. A.; Pfaltz, A.; Schreiber, J.; Eschenmoser, A.; Ankel-Fuchs, D.; Moll, J.; Jaenchen, R.; Thauer, R. K. *Helv. Chim. Acta* **1984**, *67*, 334 and references cited therein.