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Synthesis and Structure of *trans-sec,rac*-[CoL(CH₃)(H₂O)](CF₃SO₃)₂: L = 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Steric Selectivity in Alkyl Radical–Metal Radical Reactions

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Introduction

The now venerable field of cobalt macrocycle chemistry remains a lively one, at present, because of applications of these complexes to binding and catalytic reduction of carbon dioxide,[2-4] because of the fact that cobalt–carbon-bonded species of this family may serve as models for vitamin B₁₂,[5,6] and because of interesting mechanistic questions that are posed or may be addressed through studies of complexes of this class.[7]

Equatorial coordination of L (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) to a metal center gives rise to two diastereomers,[8] one racemic and one meso:

rac-L   *meso*-L
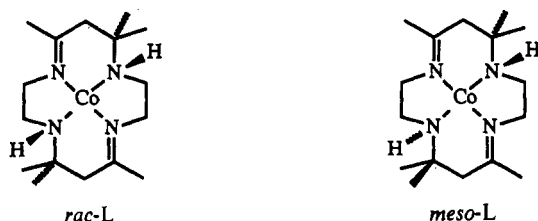
Both isomers of Co^II L^2+ have recently been structurally characterized.[9,10] In addition, when the axial coordination sites are asymmetrically occupied, two geometrical isomers containing *rac*-L are possible. This situation arises when the metal center is five-coordinate (as in the case of the cobalt(I) complex[10] CoL-(CO)⁺) or when the axial sites are occupied by two different ligands, for example X⁻ and water. If the open face is denoted "primary" and the face toward which the axial methyl groups point is denoted "secondary", the two isomers are termed primary X, aquo and secondary X, aquo.

trans-primary, *rac*   trans-secondary, *rac*   trans, *meso*
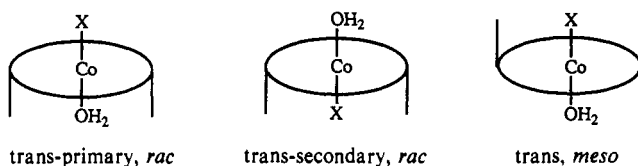
Roche and Endicott prepared and characterized both *trans,-meso*- and *trans-prim,rac*-CoL(CH₃)(H₂O)²⁺.[11,12] We used their general procedure[11,12] in the expectation of preparing the structurally characterized[13] primary isomer of the methyl complex. When the spectral properties of the product we obtained did not

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Table I. Experimental Details of the X-ray Diffraction Study of **1**

mol formula	[Co(N₄C₁₆H₃₂)(OH₂)(CH₃)](CF₃SO₃)₂
a, Å	15.340 (4)
b, Å	10.690 (3)
c, Å	18.592 (7)
β, deg	106.30 (2)
V, Å³	2926 (3)
Z	4
mol wt	670.56
space group	*P*2₁/*c*
ρ(calc), g cm⁻³	1.522
radiation	λ = 0.709 26 Å (Mo Kα)
μ, cm⁻¹	8.35
transm coeff: max; min	0.8446; 0.7037
R	0.071
*R*ᵥ	0.079
max shift/error final cycle	0.02
temp, K	295

agree with those reported for either the *meso* or the primary, racemic isomer we carried out a single-crystal X-ray diffraction study to determine the nature of the product and learned that it is the third possible geometrical isomer, the secondary, racemic complex. The structure and properties of this complex are reported in this note. Since this work was completed, a study of the substitution kinetics of the three isomers has been published.[7]

Experimental Section

Preparations. *trans-sec,rac*-[CoL(CH₃)(H₂O)](ClO₄)₂. Synthesis of this methyl complex followed the general procedure given by Roche and Endicott:[11,12] To 100 mL of deaerated 0.1 M perchloric acid was added 82 mg of [(NH₃)₅CoOC(O)CH₃](ClO₄)₂[14] and then 57.6 mg of *rac*-[CoL](ClO₄)₂.[9,15] When all of the solid had dissolved, the solution was transferred via polythene tubing to the deaerated cavity of a medium-pressure (Hanovia, immersion) mercury lamp and irradiated for 5 min. The solution was then transferred to a round-bottom flask, its volume was reduced to ca. 10 mL on a rotary evaporator, and 2 mL of concentrated perchloric acid was added. Solid (25–30 mg) formed when the solution was left overnight in the freezer. The solid was collected on a glass frit, washed three times with a few milliliters of diethyl ether, and then stored in a vacuum desiccator. About 10 mg of the solid was dissolved in ca. 0.5 mL of D₂O containing 1 M triflic acid so that the ¹H NMR spectrum of the sample could be determined; following the NMR measurements, crystals of the triflate salt (which were used in the X-ray diffraction studies, see below) formed in the NMR tube when it was left at room temperature for several days. The ¹H NMR of the sample prior to the latter "recrystallization" indicated the presence of ca. 20% of a second isomer of the complex, based on literature data,[7] the meso. Following the "recrystallization", only one isomer was present. The ¹H NMR of the latter was essentially the same in both 0.1 and 1.0 M triflic acid and is in good agreement with that recently reported by Endicott et al.:[7] δ (relative to sodium 3-(trimethylsilyl)-1-propanesulfonate, DSS) 2.315 (imine CH₃), 1.354 (equatorial CH₃), 1.120 (axial CH₃), 1.730 (Co–C-H₃). UV–vis (0.01 M HClO₄) λₘₐₓ (ε, M⁻¹ cm⁻¹) 460 nm (2.0 × 10²), 371 nm (3.6 × 10²).

Warning! The perchlorate salts used in this study are explosive and potentially hazardous.

Instrumentation. ¹H NMR spectra were determined on a Bruker AM-300 spectrometer, and UV–vis spectra were obtained on a Cary 210 spectrophotometer.

Collection and Reduction of the X-ray Diffraction Data. The crystal used for data collection, an orange plate of dimensions 0.20 × 0.37 × 0.57 mm, was mounted on the tip of a glass fiber. The diffraction data indicated monoclinic symmetry, and the systematic absences *h*0*l*, *l* = 2*n* + 1, and 0*k*0, *k* = 2*n* + 1, are consistent with the space group *P*2₁/*c* (No. 14, *C*⁵₂ₕ).[16] Crystal data and information on data collection are given in Table I and, in detail, in Table S1.

Determination and Refinement of the Structure. The structure was solved by standard Patterson heavy-atom methods. In the least-squares refinement,[17] neutral-atom scattering factors[18] and anisotropic tempera-

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Table II. Final Positional Parameters for the Non-Hydrogen Atoms in *trans-sec,rac*-[Co(N$_4$C$_{16}$H$_{32}$)(OH$_2$)(CH$_3$)](CF$_3$SO$_3$)$_2$[a]

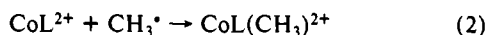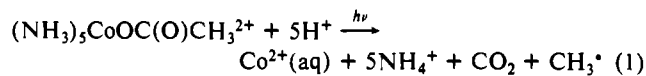| atom	x	y	z
Co	0.28207 (7)	0.17362 (10)	0.37877 (5)
O1	0.2459 (4)	0.3627 (4)	0.3719 (3)
C1	0.3154 (6)	−0.0058 (7)	0.3856 (5)
N1	0.2050 (4)	0.1595 (6)	0.4468 (3)
C2	0.2578 (6)	0.1036 (9)	0.5178 (5)
C3	0.3511 (5)	0.1641 (8)	0.5378 (4)
N4	0.3746 (4)	0.2066 (5)	0.4695 (3)
C5	0.4474 (6)	0.2697 (8)	0.4761 (4)
C5'	0.5129 (6)	0.3008 (9)	0.5491 (4)
C6	0.4692 (5)	0.3247 (8)	0.4073 (4)
C7	0.4542 (5)	0.2383 (8)	0.3388 (5)
C7'	0.5104 (6)	0.1201 (10)	0.3600 (5)
C7''	0.4869 (6)	0.3102 (10)	0.2789 (5)
N8	0.3557 (4)	0.2143 (6)	0.3103 (3)
C9	0.3255 (6)	0.1342 (9)	0.2435 (5)
C10	0.2244 (7)	0.1239 (10)	0.2228 (5)
N11	0.1890 (5)	0.1461 (6)	0.2876 (3)
C12	0.1039 (6)	0.1541 (8)	0.2798 (4)
C12'	0.0353 (7)	0.1428 (12)	0.2049 (5)
C13	0.0659 (6)	0.1857 (8)	0.3437 (4)
C14	0.1078 (5)	0.1180 (8)	0.4198 (4)
C14'	0.0570 (6)	0.1627 (9)	0.4739 (5)
C14''	0.0974 (6)	−0.0226 (8)	0.4097 (5)
S1	0.27123 (15)	−0.0132 (2)	0.04294 (12)
O11	0.2181 (5)	0.0951 (6)	0.0391 (4)
O12	0.3210 (4)	−0.0169 (6)	−0.0119 (3)
O13	0.3215 (5)	−0.0495 (7)	0.1149 (3)
C11	0.1867 (13)	−0.1357 (15)	0.0112 (10)
F11	0.2372 (9)	−0.2441 (9)	0.0161 (6)
F12	0.1389 (6)	−0.1467 (11)	0.0563 (7)
F13	0.1411 (8)	−0.1169 (12)	−0.0540 (5)
S2	0.19980 (16)	0.5174 (2)	0.20252 (12)
O21	0.1419 (4)	0.4756 (6)	0.2469 (3)
O22	0.1526 (5)	0.5532 (7)	0.1284 (5)
O23	0.2776 (5)	0.4426 (7)	0.2102 (4)
C22	0.2452 (8)	0.6634 (12)	0.2480 (6)
F21	0.3004 (5)	0.7166 (8)	0.2171 (5)
F22	0.2894 (6)	0.6428 (7)	0.3181 (4)
F23	0.1800 (6)	0.7443 (7)	0.2458 (5)

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

ture parameters were used for all non-hydrogen atoms, and the quantity $\sum w(|F_o| - |F_c|)^2$, where $w = 1.1703/(\sigma^2(F_0) + 0.0002F^2)$ was minimized. In the final cycles of refinement, hydrogen atoms were introduced in their calculated positions (X–H = 0.95 Å) and allowed to "ride" on the C or N atom to which they were bound. The hydrogen atoms on the coordinated water were located on a difference Fourier map, and their positional parameters were not varied. A common isotropic temperature factor for all of the hydrogen atoms refined to a value $U = 0.085$ (5) Å^2. After the final cycle of refinement, the R value was 0.071 and R_w was 0.079, with the largest shift being less than 0.02 of the error in the parameter.

Final non-hydrogen atomic positional parameters are given in Table II, and a list of selected interatomic distances and angles are reported in Table III. Observed and calculated structure factors (Table S2), thermal parameters for the non-hydrogen atoms (Table S3), calculated and fixed hydrogen-atom positions (Table S4), and a complete listing of bond distances and angles (Table S5) are available as supplementary material.

Results

The irradiation of (NH$_3$)$_5$CoOC(O)CH$_3$$^{2+}$ with ultraviolet light yields Co^{2+}(aq) and methyl radicals.[14] In the presence of cobalt(II) macrocycles, the methyl radicals may be scavenged and cobalt–carbon-bonded products result.[12]

$$(NH_3)_5CoOC(O)CH_3^{2+} + 5H^+ \xrightarrow{h\nu}$$
$$Co^{2+}(aq) + 5NH_4^+ + CO_2 + CH_3^{\bullet} \quad (1)$$

$$CoL^{2+} + CH_3^{\bullet} \rightarrow CoL(CH_3)^{2+} \quad (2)$$

(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1969; Vol. IV, pp 99–101, 149–150.

Table III. Selected Bond Distances and Angles in *trans-sec,rac*-[Co(N$_4$C$_{16}$H$_{32}$)(OH$_2$)(CH$_3$)](CF$_3$SO$_3$)$_2$

Distances (Å)			
Co–C1	1.980 (8)	Co–N4	1.908 (6)
Co–O1	2.090 (5)	Co–N8	1.973 (6)
Co–N1	1.966 (5)	Co–N11	1.907 (6)

Angles (deg)			
C1–Co–O1	179.5 (3)	O1–Co–N11	88.6 (3)
C1–Co–N1	94.4 (3)	N1–Co–N4	83.0 (3)
C1–Co–N4	90.4 (3)	N1–Co–N8	171.6 (3)
C1–Co–N8	94.0 (3)	N1–Co–N11	97.1 (3)
C1–Co–N11	91.3 (3)	N4–Co–N8	96.4 (3)
O1–Co–N1	85.2 (2)	N4–Co–N11	178.2 (3)
O1–Co–N4	89.7 (2)	N8–Co–N11	83.2 (3)
O1–Co–N8	86.4 (2)		
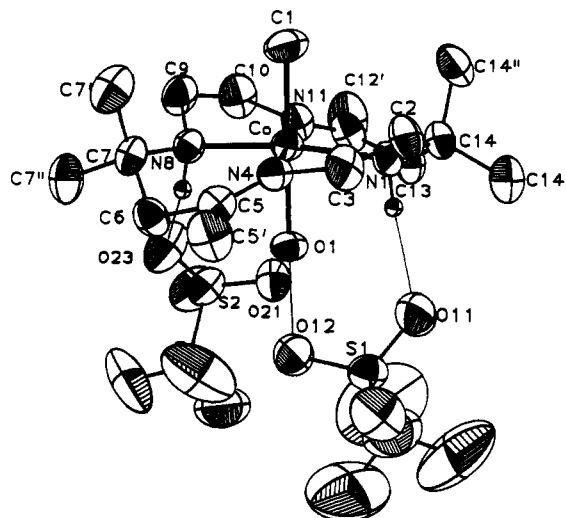
Figure 1. ORTEP view of *trans-sec,rac*-[Co(N$_4$C$_{16}$H$_{32}$)(CH$_3$)(OH$_2$)](CF$_3$SO$_3$)$_2$ with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted except for the amine hydrogens of N1 and N8. It can be seen that the macrocycle is twisted so that the two "axial" methyl groups of the macrocycle are swept back away from the axially coordinated methyl ligand. This configuration is stabilized by hydrogen bonding (very thin lines) between the macrocycle N1 and N8 amine hydrogen atoms and two oxygen atoms on the two crystallographically independent trifluoromethanesulfonate anions. Further stabilization is contributed by hydrogen bonds between the axial water ligand and two other oxygen atoms on the trifluoromethanesulfonate anions.

These reactions were first used as the basis of a synthetic strategy for the preparation of *trans,meso*-CoL(CH$_3$)(H$_2$O)$^{2+}$. (The procedure is also successful with the hydroxymethyl radical replacing the methyl radical.[19]) Here we have found that the procedure is also applicable with *rac*-CoL^{2+} as starting material. The yield ($\leq$ca. 50%) of the initially isolated perchlorate salt is, however, rather low, in part because of its high solubility in water. Recently[6] *trans*-Co(dimethylglyoximato)$_2$(OH$_2$)CH$_3$ has been used as the methyl radical source in a photochemical procedure analogous to that above. Both *meso* and secondary, *rac* isomers of CoL(CH$_3$)(H$_2$O)$^{2+}$ have been synthesized by this route.[7] For the latter isomer, the yields appear to be comparable via the two routes. However, the amounts that can be prepared in a single run via the method we used are limited by the relatively low solubility of the cobaltammine.

Description of the Structure. In Figure 1, a view of the Co-(N$_4$C$_{16}$H$_{32}$)(CH$_3$)(OH$_2$)](CF$_3$SO$_3$)$_2$ unit is presented. The usual numbering scheme is used for the 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene macrocycle L. The cobalt(III) center is six-coordinate, with the four nitrogens of the macrocycle forming the equatorial plane and trans H$_2$O and CH$_3^-$ ligands occupying the axial positions. The macrocycle is in the

(19) Chou, M. H.; Creutz, C.; Szalda, D. J. *Inorg. Chem.*, to be submitted for publication.

L
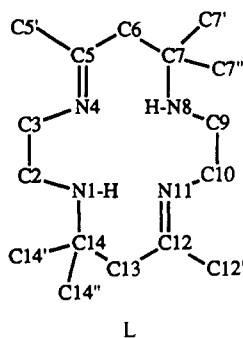
racemic form, with the two amine (N1 and N8) hydrogens on the same side as the aquo ligand. Thus the two axial macrocycle methyl groups are on the same face as the methyl ligand. This is the so-called secondary isomer of the methyl, aquo complex. The $[CoL(CH_3)(OH_2)](CF_3SO_3)_2$ unit is stabilized by two sets of hydyrogen bonds (Table S6) between two of the oxygen atoms on each triflate anion and the hydrogen atoms of a macrocycle N–H and the axially coordinated water molecule. Analogous hydrogen-bonding interactions were found[9] to be important for the five-coordinate cobalt(II) complexes $prim,rac$-$CoL(OH_2)^{2+}$ and $prim,rac$-$CoL(OClO_3)^+$. These hydrogen-bonding interactions, as well as methyl–methyl repulsion on the secondary face of the macrocycle, cause a folding of the macrocycle toward the axial water ligand and away from the axial methyl ligand. The fold, defined as the angle between the N1, N4, N8, and the N1, N8, N11 planes, is 6.8°.

Some qualitative experiments were carried out in order to compare the reactivity of sec,rac-$CoL(CH_3)(OH_2)^{2+}$ with its isomers. In these, evidence was found that SCN^- rapidly[7] replaces the axial water molecule to give a SCN^- adduct with $\lambda_{max} = 450$ and 365 nm in 0.01 M $HClO_4$. No evidence was found for Cl^-, Br^-, or I^- binding ($K \leq 10$ M^{-1}). Treatment of the crude mixture of sec,rac-$CoL(CH_3)(OH_2)^{2+}$ (80%) and $meso$-$CoL(CH_3)(OH_2)^{2+}$ with 0.01 M carbonate buffer (pH 10.3 in D_2O, followed by reacidification to pH 1.6, yielded a mixture ca. 20% in the primary rac isomer with the secondary, rac isomer remaining unchanged. Given that $meso$-to-primary, rac isomerization is known to occur readily[12] and that the primary, rac isomer is favored 5:1 over the $meso$ isomer at equilibrium,[7] we must conclude that the secondary, rac/primary, rac equilibrium is slow under these conditions.

Discussion

The structure of the secondary isomer of rac-$CoL(CH_3)(OH_2)^{2+}$ may be compared with that determined by Heeg et al. for the primary isomer.[13] The Co–C bond distances are the same (1.980 (8) vs 1.971 (6) Å), but the Co–OH_2 distance is 0.025 (5) Å shorter in the secondary (2.090 (5) Å) than in the primary (2.115 (4) Å) isomer. There are no significant differences between the two isomers in the intramacrocycle bond distances. However, the macrocycle folding described above for the secondary isomer is responsible for differences in the bond angles. (The fold angle is only 3.1° in the primary isomer.) The largest difference is seen in the N_{am}–Co–N_{am} angle, which is 179.0 (3)° in the primary isomer and 171.6 (3)° in the secondary isomer. The cobalt atom lies 0.087 Å out of the plane of the four nitrogen atoms toward the axial methyl ligand in the secondary isomer compared with 0.009 Å in the primary isomer, and the axial methyl groups are more swept back in the former due to the larger volume of the axially coordinated methyl ligand.

As was mentioned previously,[9] the most remarkable aspect of this study is the fact that reaction of rac-CoL^{2+} with methyl radicals results in Co–C bond formation at the sterically hindered, secondary face of the macrocycle rather than at the sterically accessible primary face. This is particularly remarkable in light of the relatively small rate constant for $CH_3^{\bullet}$ addition to rac-CoL^{2+}, $k = 0.6 \times 10^8$ M^{-1} s^{-1}; this is to be compared to $k = 2.3 \times 10^8$ M^{-1} s^{-1} for $CH_3^{\bullet}$ addition to $meso$-CoL^{2+}.[20,21] We take this to be strong evidence that the dominant form of rac-CoL^{2+} is actually five-coordinate prim, rac-$CoL(H_2O)^{2+}$ in aqueous

solution. Since no ($\leq 10\%$) primary isomer is formed, the rate constant for addition to the primary face of rac-CoL^{2+} must be $\leq 0.6 \times 10^7$ M^{-1} s^{-1}. Thus it would appear that water exchange is at least 40 times slower for the primary site of rac-$CoL(H_2O)^{2+}$ than for $meso$-$CoL(H_2O)_2^{2+}$ (assuming that the dominant form is six-coordinate, as implicated by structural work on the solid state[22]). This is qualitatively consistent with the trend seen in the crystallographically determined Co(II)-OH_2 distances, 2.25 (5) (primary, rac)[9] and 2.482 (5) Å ($meso$).[22]

Acknowledgment. We thank Dr. M. Perkovic for helpful comments and M. H. Chou for preparing the sample used in the structural studies. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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Barrier to Internal Rotation in a Heterometallic Tetrahedrane Cluster. NMR Evidence for Metal Cluster–Aryl Orbital Overlap

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In earlier reports from this laboratory,[2–4] we have demonstrated the utility of ^{13}C NMR spin–lattice relaxation times[5] as a sensitive probe of the electronic and steric factors affecting the internal rotational dynamics of the phenyl groups in benzylidyne- and phosphinidene-capped metal carbonyl clusters.

Several years ago, Schilling and Hoffmann[6] predicted, theoretically, that the barrier to internal rotation of the capping group should be small to nonexistent in trimetallic clusters of the type $[Co_3(CO)_9(\mu_3\text{-}CCR_2)^+]$ (where R = H, alkyl), which contain only terminal carbonyls. We were able to verify this prediction experimentally in a recent NMR relaxation time study[3] of the protonated phenyl carbons in the complex $Co_3(CO)_9(\mu_3\text{-}CPh)$ as a function of temperature in the solvent chloroform. It was observed that "spinning" of the aryl ring about the C–C bond is

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