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Solution Studies of the Cobalt(II) *N-rac*- and *N-meso*-CoL^{2+} Isomers and Molecular and Crystal Structures of the Low-Spin, Five-Coordinate Cobalt(II) Macrocyclic Complexes *N-rac*-$[CoL(H_2O)](ClO_4)_2 \cdot 0.6H_2O$ (1) and *N-rac*-$[CoL(OClO_3)]ClO_4$ (2) (L = 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)

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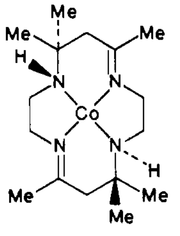
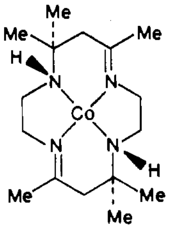
The title cobalt(II) complexes were prepared from the reaction of $CoL(Cl)H_2O^{2+}$ with $Cr^{2+}(aq)$ in 1.0 M $HClO_4$, and crystals of **1** and **2** were obtained from acetone. Structures were determined from single-crystal X-ray diffraction data collected with use of Cu Kα radiation. Crystallographic data: **1**, *N-rac*-$[CoL(H_2O)](ClO_4)_2 \cdot 0.6H_2O$, *Pbcn*, $a = 15.654$ (4) Å, $b = 14.623$ (2) Å, $c = 55.221$ (11) Å, $V = 12640$ (7) Å^3, $Z = 20$ ($R = 0.113$, $R_w = 0.135$); **2**, *N-rac*-$[CoL(OClO_3)]ClO_4$, $P2_1/c$, $a = 10.336$ (3) Å, $b = 17.094$ (1) Å, $c = 13.890$ (2) Å, $\beta = 105.59$ (2)°, $V = 2363$ (1) Å^3, $Z = 4$ ($R = 0.061$, $R_w = 0.087$). Both **1** and **2** contain a five-coordinate cobalt(II) center with the four nitrogen atoms of *N-rac*-L forming the base of a square pyramid and axial water (**1**, $Co–OH_2 = 2.25$ (5) Å) or axial perchlorate ion (**2**, $Co–OClO_3 = 2.305$ (5) Å) forming the apex of the square pyramid. Studies of *N-rac*- and *N-meso*-CoL^{2+} in solution (perchlorate salts) are described: the lowest energy d–d band (1400–1700 nm, depending upon solvent) provides a probe of the isomeric composition of the solutions, since this band is 2–3 times more intense for the *N-rac* than for the *N-meso* isomer. Equilibration of the two isomers is slow at room temperature ($<2 \times 10^{-7}$ s^{-1}) in organic solvents and in acidic aqueous solutions; it is, however, rapid in alkaline media, and the *N-rac* isomer is favored at equilibrium.

Introduction

Equatorial coordination of the title 14-membered tetraaza macrocycle[2] L to a metal center gives rise to two diastereomers, N-meso and N-racemic.[3] Both isomers of NiL^{2+} have been structurally characterized[4] as have those of a few (six-coordinate) cobalt(III) complexes[5-7] and (five-coordinate) cobalt(I) complexes[8,9] such as $[CoL(CO)]ClO_4$. By contrast, all structurally characterized cobalt(II) complexes[5,6,9] of this macrocycle reported to date contain the *N-meso* isomer. The structure of the *N-rac* isomer is of considerable interest in the context of electron-transfer studies, in which knowledge of the structural differences between Co(II) and Co(III) complexes is important to an understanding of both outer-sphere and inner-sphere electron-exchange rates.[10] In addition, such structural characterization is important to an understanding of the dynamics of the low-spin d^7 CoL^{2+} solution chemistry, since both diastereomers may be present and undergo substitutional, redox, or radical-addition chemistry.[11-13] Solid perchlorate salts of the *N-rac* Co(II) complex were first prepared[14] in the course of studies of inner-sphere self-exchange reactions, and crystals of *N-rac*-$[CoL(H_2O)](ClO_4)_2 \cdot 0.6H_2O$ (**1**) and *N-rac*-$[CoL(OClO_3)]ClO_4$ (**2**) were ultimately grown by slow solvent evaporation from acetone solutions. The preparation and structures of **1** and **2** are reported here. In addition, we describe results of solution spectroscopic studies of the two isomers, which have led to the determination of the rate and equilibrium constants for the *N-meso*/*N-rac* interconversion.



N-meso



N-rac

Experimental Section

Preparation of *N-rac*-$[CoL(H_2O)](ClO_4)_2$. The procedure used[14] was a variation of that reported[6] for the *N-meso* isomer. To deaerated solid (~0.2 g) *N-rac*-$[CoL(X)(H_2O)](ClO_4)_2$ (X = Cl or Br)[15] was added a minimum volume (~15 mL) of deaerated 1.0 M aqueous perchloric acid. To the resulting solution was added 5.0 mL of 0.2 M aqueous $Cr(ClO_4)_2$ in 1 M $HClO_4$. The solution was immediately cooled in an ice bath, and yellow solid usually started to form. If solid formation was not observed after a few minutes, solid sodium perchlorate was added. The yellow solid was collected on a glass frit and washed with a minimum volume of cold 1.0 M $HClO_4$ and then diethyl ether. The solid (yield ~0.1 g) was dried at 50 °C under vacuum overnight; it decomposes if not completely dry. *Warning!* The perchlorate salts used in this study are explosive and potentially hazardous.

In our hands, the published procedure of Goedken et al.[16] gave the same *N-rac* material. The *N-meso* isomer used here was prepared as described by Rillema et al.[17]

Near-infrared spectra were measured on a Cary 17 spectrophotometer, and IR spectra were measured on a Nicolet MX-1 FTIR spectrophotometer. The solutions used in the near-IR studies were prepared under argon with CH_3CN, perdeuterated acetone, or D_2O and measured against a solvent reference. The use of dry samples was essential because water O–H overtones interfere with the accurate measurement of the

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Table I. Experimental Details of the X-ray Diffraction Study of **1** and **2**

	1	**2**
mol formula	$[Co(N_4C_{16}H_{32})(H_2O)](ClO_4)_2{\cdot}0.6H_2O$	$[Co(N_4C_{16}H_{32})ClO_4]ClO_4$
a, Å	15.654 (4)	10.336 (3)
b, Å	14.623 (2)	17.094 (1)
c, Å	55.221 (11)	13.890 (2)
β, deg		105.59 (2)
V, Å^3	12640 (7)	2363 (1)
Z	20	4
mol wt	567.11	538.29
space group	*Pbcn*	$P2_1/c$
ρ(calc), g cm^{-3}	1.490	1.512
radiation	Cu Kα (λ = 1.54051 Å)	Cu Kα (λ = 1.54051 Å)
μ, cm^{-1}	76.3	80.4
transmission coeff: max, min	0.2998, 0.1095	0.2332, 0.10539
R	0.113	0.061
R_w	0.135	0.087
max shift/error, final cycle	≤0.03	≤0.01
temp, K	294	295

weak d–d absorptions. ESR spectra were recorded on a Bruker-IBM ER200D spectrometer equipped with a field frequency lock, a variable temperature control unit, and an Aspect 2000 data system. The measurements were done at 130 K in frozen CH_3CN solutions that were prepared under vacuum. The perchlorate salts were used in all the work reported here.

Collection and Reduction of X-ray Data. The crystals of $[CoL(H_2O)](ClO_4)_2$ (**1**) and $[CoL(ClO_4)](ClO_4)$ (**2**) were isolated from two different crystallization procedures of *N-rac*-$[Co(L)(H_2O)](ClO_4)_2$. Crystals of **1** were prepared by dissolving ~30 mg of the compound in acetone (3–5 mL) and gently blowing a stream of water-saturated argon over the acetone solution. Crystals formed after about 1.5 h. Crystals of **2** were prepared by dissolving ~200 mg of the compound in ~20 mL of acetone in a beaker and placing this beaker in a desiccator containing Drierite. The desiccator was evacuated, and the solution was allowed to slowly evaporate, with occasional evacuation of the desiccator. Crystals formed in about 3 days.

$[Co(N_4C_{16}H_{32})OH_2](ClO_4)_2{\cdot}0.6H_2O$ (1) crystallizes as orange prisms. A crystal 0.19 × 0.33 × 0.45 mm was coated with petroleum jelly and mounted in a glass capillary. The diffraction data showed orthorhombic symmetry, and the systematic absences $0kl$ ($k = 2n + 1$) $h0l$ ($l = 2n + 1$) and $hk0$ ($h + k = 2n + 1$) were consistent with the space group *Pbcn* (No. 60).[18a] $[Co(N_4C_{16}H_{32})ClO_4]ClO_4$ (**2**) crystallizes as large orange prisms. One large crystal was cut into several smaller pieces for study by X-rays. A piece of approximate dimensions 0.47 × 0.30 × 0.30 mm was coated with petroleum jelly, mounted in a glass capillary, and used for data collection. The diffraction data indicated monoclinic symmetry with systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) consistent with the space group $P2_1/c$ (No. 14).[18a]

Crystal data and the details of data collection are given in Table I and Table S1 (supplementary material).

Determination and Refinement of the Structures. The structure of **1** was solved by direct methods,[19] which indicated the positions of the cobalt atoms. The other non-hydrogen atoms were located on difference Fourier maps. There are 2.5 cobalt complexes, five perchlorate anions, and 1.5 waters per asymmetric unit in **1**. Because of the small number of reflections with $F_o \geq 3\sigma(F)$, anisotropic thermal parameters were used for the cobalt and chloride atoms and individual isotropic temperature parameters were used for the other non-hydrogen atoms. A common isotropic temperature parameter was refined for all of the hydrogen atoms (the hydrogen atoms of the water were not located), which were placed at calculated[19] positions (X–H = 0.95 Å) and allowed to "ride" on the C or N atoms to which they were attached. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinements with use of neutral atom scattering factors.[18b] The structure of **2** was solved by the standard Patterson,[19] heavy-atom technique. The refinement procedure was the same as for **1**, except that anisotropic temperature parameters were used for all of the non-hydrogen atoms.

Final non-hydrogen atomic positional parameters for **1** and **2** are given in Tables II and III, and selected interatomic distances and angles are listed in Table IV. The standard atom-numbering scheme is used for the macrocycle.[9] Additional material is provided in Tables S1–S11 and Figure S1 (supplementary material).

Results and Discussion

Description of the Structures. In **1**, the structures of three independent Co units are essentially the same, although one unit is at a special position (see below). Both **1** and **2** contain a five-coordinate Co(II) center with the four nitrogens of the macrocycle forming the base of a square pyramid. In **1** a water molecule ($Co–OH_2$ = 2.25 (5) Å, average) and in **2** an oxygen of a perchlorate anion (Co–O = 2.305 (5) Å) occupy the apex of the square pyramid. Since the parameters within the two complexes are almost identical, complex **2** will be discussed in detail because of the higher quality of its refinement. The minor differences between the two complexes will be highlighted. Views of **1** and **2** are presented in Figure 1. As can be seen in these views, the sixth (axial) coordination site is essentially blocked by the two axial methyl groups of the macrocycle (C(methyl)–C(methyl) distance 4.3 Å and Co–C(methyl) distance 3.06–3.3 Å, Table V). The amine hydrogens of the macrocycle are both on the same side of the macrocycle as the axial ligand; these are the "primary" isomers. In **1** the amine hydrogens and the axial water molecule form hydrogen bonds to two unique perchlorate ions (O···O distances average 2.98 (6) Å and N···O distances average 3.19 (5) Å) in the lattice (Figure 1), thus helping to stabilize crystals of the racemic form of the complex; in **2**, one amine hydrogen forms an intermolecular hydrogen bond to a noncoordinated perchlorate anion, while the other forms an intramolecular hydrogen bond to the coordinated perchlorate ion (N···O distances average 3.008 (8) Å) (Table S10 and Figure 1, bottom).

Differences in the hydrogen-bonding interactions due to the waters of crystallization among the three crystallographically independent complexes in **1** (Table S11, Figure S1) provide an explanation for the fact that there are 2.5 molecules per asymmetric unit. In the two complexes in general positions , the axial water molecule is hydrogen-bonded to two perchlorate anions, while in the complex in the special position, the axial water molecule is hydrogen-bonded to two perchlorate anions and accepts two hydrogen bonds from two lattice water molecules. The molecules in general positions have approximate 2-fold symmetry while the molecule in the special position has crystallographic 2-fold symmetry, with the cobalt atom and oxygen atom of the axial water molecule situated on a 2-fold axis.

Structural Comparisons. The axial Co–O bond distances in **1** and **2** (2.25 (5) and 2.305 (5) Å) are essentially identical, suggesting that the conformation of the ligand in these complexes is such that it minimizes steric effects on this side of the macrocycle. The axial Co–O bonds in **1** and **2** are shorter than those in the six-coordinate *N-meso* diaquo complex[6] of this ligand (2.482 (5) Å) and about the same as that (2.283 (9) Å)[20] in [Co(12,14-dimethyl-1,4,8,11-tetraazacyclotetradecane-11,13-di-

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Table II. Final Positional Parameters for the Non-Hydrogen Atoms in $[Co(N_4C_{16}H_{32})(H_2O)](ClO_4)_2\cdot 0.6H_2O$ (**1**)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co1	0.1179 (4)	0.2649 (4)	0.44620 (10)	C2B	0.615 (2)	0.365 (2)	0.1497 (6)
O11	0.1970 (18)	0.3771 (18)	0.4655 (5)	C2C	0.598 (3)	0.522 (3)	0.1669 (7)
N11	0.0105 (19)	0.298 (2)	0.4628 (6)	Co3	0.5000	−0.1494 (5)	0.2500
C12	−0.030 (3)	0.362 (3)	0.4478 (9)	O31	0.5000	0.002 (2)	0.2500
C13	0.031 (3)	0.414 (3)	0.4314 (8)	N31	0.4598 (16)	−0.1554 (17)	0.2833 (4)
N14	0.090 (2)	0.350 (2)	0.4210 (6)	C32	0.534 (2)	−0.179 (2)	0.2998 (6)
C15	0.127 (3)	0.361 (3)	0.3978 (8)	C33	0.607 (2)	−0.131 (3)	0.2886 (6)
C15′	0.097 (3)	0.433 (3)	0.3827 (8)	N34	0.6178 (16)	−0.1513 (16)	0.2634 (5)
C16	0.186 (2)	0.302 (2)	0.3908 (6)	C35	0.683 (3)	−0.160 (3)	0.2492 (8)
C17	0.196 (2)	0.211 (3)	0.4007 (7)	C35′	0.770 (2)	−0.159 (3)	0.2643 (7)
C17′	0.120 (2)	0.146 (2)	0.3982 (6)	C36	0.690 (2)	−0.189 (3)	0.2252 (7)
C17″	0.271 (3)	0.164 (3)	0.3873 (9)	C37	0.612 (2)	−0.222 (2)	0.2131 (6)
N18	0.2166 (15)	0.2180 (16)	0.4286 (4)	C37′	0.637 (2)	−0.230 (2)	0.1866 (6)
C19	0.250 (3)	0.132 (3)	0.4398 (7)	C37″	0.584 (2)	−0.315 (2)	0.2242 (7)
C110	0.233 (3)	0.141 (3)	0.4642 (7)	Cl1	0.3548 (10)	0.0685 (11)	0.3175 (3)
N111	0.146 (2)	0.182 (2)	0.4698 (6)	O111	0.428 (2)	0.036 (2)	0.3065 (6)
C112	0.104 (3)	0.155 (3)	0.4876 (9)	O112	0.312 (3)	0.008 (3)	0.3293 (8)
C1A	0.128 (3)	0.092 (3)	0.5098 (8)	O113	0.302 (4)	0.071 (4)	0.2998 (12)
C113	0.019 (3)	0.178 (3)	0.4944 (7)	O114	0.363 (3)	0.144 (4)	0.3258 (10)
C114	−0.037 (3)	0.225 (3)	0.4731 (8)	Cl2	0.1080 (9)	0.2719 (12)	0.1297 (2)
C1B	−0.055 (2)	0.154 (2)	0.4556 (7)	O221	0.027 (2)	0.2542 (19)	0.1393 (5)
C1C	−0.112 (3)	0.255 (3)	0.4852 (8)	O222	0.171 (3)	0.213 (3)	0.1379 (8)
Co2	0.4104 (4)	0.3212 (4)	0.14660 (10)	O223	0.141 (4)	0.347 (4)	0.1399 (11)
O21	0.2909 (14)	0.3701 (14)	0.1645 (4)	O224	0.101 (4)	0.250 (4)	0.1079 (10)
N21	0.4669 (16)	0.4359 (16)	0.1537 (4)	Cl3	0.4109 (9)	0.3897 (9)	0.4377 (2)
C22	0.468 (2)	0.492 (3)	0.1304 (6)	O331	0.382 (3)	0.437 (3)	0.4573 (8)
C23	0.389 (2)	0.476 (2)	0.1181 (6)	O332	0.347 (3)	0.404 (3)	0.4205 (8)
N24	0.3751 (19)	0.379 (2)	0.1162 (6)	O333	0.405 (3)	0.295 (4)	0.4432 (9)
C25	0.339 (3)	0.332 (3)	0.0981 (8)	O334	0.494 (4)	0.416 (4)	0.4335 (9)
C25′	0.305 (3)	0.391 (3)	0.0772 (7)	Cl4	0.1749 (10)	0.0783 (10)	0.2029 (3)
C26	0.327 (2)	0.237 (2)	0.0958 (6)	O441	0.237 (3)	0.026 (3)	0.1925 (8)
C27	0.381 (2)	0.176 (3)	0.1126 (7)	O442	0.190 (3)	0.165 (4)	0.2046 (8)
C27′	0.350 (2)	0.078 (2)	0.1086 (7)	O443	0.098 (4)	0.060 (3)	0.1965 (9)
C27″	0.4759 (19)	0.182 (2)	0.1076 (5)	O444	0.141 (5)	0.044 (5)	0.2206 (15)
N28	0.3622 (16)	0.2003 (16)	0.1387 (4)	Cl5	0.3436 (16)	0.0961 (14)	0.0273 (3)
C29	0.391 (3)	0.130 (3)	0.1565 (6)	O551	0.424 (3)	0.102 (4)	0.0418 (10)
C210	0.402 (3)	0.185 (3)	0.1813 (7)	O552	0.405 (4)	0.064 (4)	0.0073 (11)
N211	0.4443 (16)	0.2681 (18)	0.1774 (5)	O553	0.333 (4)	0.179 (4)	0.0227 (10)
C212	0.490 (2)	0.301 (2)	0.1921 (7)	O554	0.310 (4)	0.034 (5)	0.0388 (13)
C2A	0.507 (3)	0.256 (3)	0.2188 (7)	O1	0.1532 (17)	0.6005 (19)	0.2482 (5)
C213	0.543 (2)	0.386 (2)	0.1905 (7)	O2	0.0000	−0.032 (5)	0.2500
C214	0.554 (2)	0.430 (3)	0.1642 (6)				

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

ene)$OH_2](PF_6)_2$ (in which the sixth position is occupied by a weak Co–F (2.559 (10) Å) bond) and the 2.289 (15) Å found in the six-coordinate $Co[([14]tetraeneN_4)(OH_2)_2](ClO_4)_2$.[20]

An interesting comparison can be made between **2** and the previously reported complex[8] $[(CoL)_2CO_2H]^{3+}$. In the latter, one cobalt is coordinated to an oxygen of the CO_2H group with a Co–O distance of 2.28 (3) Å, and there is an intramolecular hydrogen bond between an amine hydrogen and the noncoordinated oxygen atom. A similar situation is observed in **2**, where one oxygen of the perchlorate is coordinated to the cobalt and another forms an intramolecular hydrogen bond to an amine hydrogen on the macrocycle.

The Co–N bond distances and the bond distances within the macrocycle in both **1** and **2** are similar to those reported in other structures[9] containing this macrocycle.

Spectroscopic Comparison of the *N-rac* and *N-meso* Isomers. As noted earlier, knowledge of the isomeric composition of CoL^{2+} solids and solutions is important to an interpretation of CoL^{2+} reactivity. Thus, there has been a need for experimental criteria (apart from X-ray crystallography) of isomeric purity.

Solids. We have found IR spectra of the perchlorate salts to provide a reliable means of distinguishing the two diastereomers in the solid state. The critical 1500–1200-cm^{-1} region[14] is shown in Figure 2. The 1308-cm^{-1} (*N-rac*) and 1300-cm^{-1} (N-*meso*) peaks are particularly useful.

Solutions. EPR spectra of frozen solutions of the two isomers exhibit axial symmetries. Perpendicular components have $g = 2.43$ (*N-meso*) and $g = 2.45$ (*N-rac*); parallel components, which split into eight lines due to hyperfine interaction with the Co nuclear spin ($I = {}^7/_2$), have $g = 2.02$ (*N-meso*) and $g = 2.01$ (*N-rac*). The *N-rac* spectrum we obtained is similar to that reported[16] by Goedken et al. except that we observed the hyperfine structure around $g = 2.25$ as only a shoulder. By contrast, the perpendicular component of the *N-meso* isomer is featureless.

In solution, the most useful probe of diastereomeric composition (apart from chemical methods[21]) appears to be the intensity of the solvent-dependent d–d band found in the 1400–1700-nm region and the position of a UV band at 310–330 nm. (See Table VI.) In all cases, the near-IR band maxima are nearly the same for the two isomers but, as found[3] for NiL^{2+}, the molar absorptivities are greater for the *N-rac* than for the *N-meso* isomer. The maxima shift with solvent, and interestingly, the intensities increase as the band moves to higher energy.

Although our values for *N-rac*-CoL^{2+} in aqueous media (D_2O) differ somewhat from those reported by Goedken et al.[16] (possibly because the earlier samples were contaminated with H_2O), the solid-state IR spectrum of the compound obtained by the route given in ref 16 is the same as that determined for the *N-rac*

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(21) (a) The reaction of *N-meso*-CoL^{2+} with CH_3 radical yields *N-meso*-$CoL(CH_3)(H_2O)^{2+}$.[11] In contrast, the reaction of *N-rac*-CoL^{2+} with CH_3 radicals[1f] in 0.1 M $HClO_4$ yields[21b] the "secondary" *N-rac* isomer of $CoL(CH_3)(H_2O)^{2+}$ (i.e., the methyl ligand is bound on the face toward which the axial methyl groups "point"). The most reasonable explanation for the formation of the secondary, rather than the primary,[7] isomer of the methyl adduct is that bound water blocks the primary face of the macrocycle in the *N-rac* complex so that only the secondary face is kinetically accessible to the methyl radical. (b) Szalda, D. J.; Schwarz, C. L.; Creutz, C. Unpublished results.

Table III. Final Positional Parameters for the Non-Hydrogen Atoms in $[Co(N_4C_{16}H_{32})(ClO_4)]ClO_4$ (**2**)[a]

atom	*x*	*y*	*z*
Co1	0.25232 (10)	0.40380 (6)	0.24152 (7)
N1	0.1532 (6)	0.3101 (3)	0.1798 (4)
C2	0.2038 (7)	0.2865 (4)	0.0931 (5)
C3	0.3507 (8)	0.3044 (4)	0.1173 (6)
N4	0.3711 (6)	0.3850 (3)	0.1598 (4)
C5	0.4708 (7)	0.4251 (4)	0.1501 (5)
C5′	0.5712 (10)	0.3956 (5)	0.0970 (8)
C6	0.5004 (7)	0.5044 (4)	0.1966 (5)
C7	0.3899 (7)	0.5514 (4)	0.2235 (5)
C7′	0.4533 (9)	0.6270 (5)	0.2745 (6)
C7″	0.2785 (9)	0.5689 (5)	0.1301 (5)
N8	0.3374 (6)	0.5034 (3)	0.2943 (4)
C9	0.2454 (8)	0.5442 (4)	0.3416 (5)
C10	0.1873 (9)	0.4856 (5)	0.3980 (6)
N11	0.1336 (6)	0.4221 (3)	0.3264 (4)
C12	0.0258 (8)	0.3859 (4)	0.3285 (6)
C12′	−0.0509 (10)	0.4032 (5)	0.4033 (6)
C13	−0.0331 (8)	0.3255 (5)	0.2535 (6)
C14	0.0048 (7)	0.3217 (5)	0.1553 (6)
C14′	−0.0699 (9)	0.2530 (6)	0.0958 (8)
C14″	−0.0299 (8)	0.3970 (5)	0.0967 (6)
Cl1	0.5326 (2)	0.33636 (11)	0.41181 (14)
O11	0.3900 (5)	0.3299 (3)	0.3667 (4)
O12	0.5644 (8)	0.4162 (4)	0.4365 (6)
O13	0.6030 (8)	0.3152 (5)	0.3416 (6)
O14	0.5722 (6)	0.2887 (4)	0.4982 (4)
Cl2	0.1626 (12)	0.39567 (11)	0.82394 (17)
O21	0.2443 (9)	0.4323 (5)	0.9111 (6)
O22	0.0413 (8)	0.3682 (6)	0.8414 (6)
O23	0.2350 (8)	0.3354 (5)	0.8006 (9)
O24	0.1348 (10)	0.4486 (7)	0.7497 (7)

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

Table IV. Selected Bond Distances and Angles in $[Co(N_4C_{16}H_{32})(H_2O)](ClO_4)_2{\cdot}0.6H_2O$ (**1**)[a] and $[Co(N_4C_{16}H_{32})(ClO_4)]ClO_4$ (**2**)

1		2	
	Bond Distances (Å)		
Co–O1	2.25 (5)	Co–O11	2.305 (5)
Co–N1	1.95 (2)	Co–N1	1.968 (6)
Co–N4	1.96 (3)	Co–N4	1.910 (6)
Co–N8	1.96 (1)	Co–N8	1.965 (5)
Co–N11	1.88 (8)	Co–N11	1.943 (6)
	Bond Angles (deg)		
O1–Co–N1	92 (1)	O11–Co–N1	91.5 (2)
O1–Co–N4	90 (1)	O11–Co–N4	89.5 (2)
O1–Co–N8	93 (1)	O11–Co–N8	94.0 (2)
O1–Co–N11	90 (1)	O11–Co–N11	89.6 (2)
N1–Co–N4	87 (1)	N1–Co–N4	86.9 (2)
N1–Co–N8	174 (1)	N1–Co–N8	174.4 (2)
N1–Co–N11	92 (1)	N1–Co–N11	93.2 (2)
N4–Co–N8	94 (1)	N4–Co–N8	94.2 (2)
N4–Co–N11	178 (1)	N4–Co–N11	179.1 (2)
N8–Co–N11	86 (1)	N8–Co–N11	85.8 (2)

[a] Average over the 2.5 molecules in the asymmetric unit.

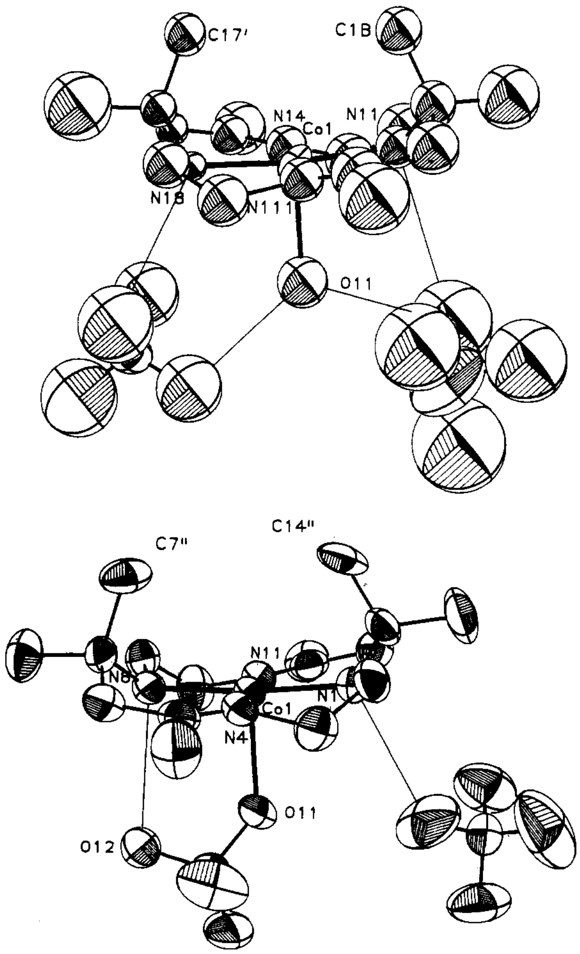

Figure 1. (Top) ORTEP view of *N-rac*-$[Co(N_4C_{16}H_{32})H_2O](ClO_4)_2$ with thermal ellipsoids at the 50% probability level (hydrogen atoms omitted). Two unique perchlorate ions are associated with each cobalt complex by a pair of hydrogen bonds (very thin lines), one from the axial water molecule (O···O distance 2.73 (6)–3.36 (4) Å) and one from the amine (N···O distance 3.00 (5)–3.45 (5) Å) of the macrocycle. In this way the perchlorate anions stabilize the racemic form of the complex. The two axial methyl groups (C17′···C1B distance 4.07 Å) essentially block the sixth coordination site; Co–C(methyl) distances are 3.13 and 3.19 Å. (Bottom) ORTEP view of *N-rac*-$[Co(N_4C_{16}H_{32})OClO_3](ClO_4)$. The hydrogens are omitted, and the thermal ellipsoids are at the 50% probability level. There is an intramolecular hydrogen bond (very thin lines) between the amine of the macrocycle N8 and an oxygen of the coordinated perchlorate anion (N···O distance 3.022 (8) Å) and an intermolecular hydrogen bond between the other amine, N1, and the uncoordinated perchlorate anion (N···O distance 2.993 (8) Å). The C7″···C14″ distance is 4.27 Å, and the Co–C(methyl) distances are 3.06 and 3.26 Å.

compound. Thus, the method in ref 16 gives the *N-rac* isomer as the primary product, and the series of five-coordinate species described by Goedken et al. is based on the *N-rac* isomer. In contrast, the procedure of Rillema et al.[17] gives the *N-meso* isomer

Table V. Comparison of Averaged Parameters in Complexes Containing *rac*-L

complex	$Co–X_{ax}$, Å	$Co–Me_{ax}$, Å	$Me_{ax}···Me_{ax}$, Å	$Co–N_{am}$, Å	$Co–N_{im}$, Å	δ,[j] Å
$CoL(OClO_3)^+$	2.305 (5)	3.06 3.26	4.27	1.967 (6)	1.926 (6)	0.04[e]
$CoL(H_2O)^{2+}$	2.25 (5)	3.13 3.19	4.07	1.95 (2)	1.93 (3)	0.05[e]
$(CoL)_2(CO_2H)^{3+}$	2.28 (3)[a] 2.06 (6)[b]	3.12 3.32	4.32	1.91	1.93	0.10[f]
$CoL(CO)^+$	1.797 (10)	3.76	5.49	2.158 (5)	2.075 (5)	0.57[g]
$CoL(CH_3)(H_2O)^{2+}$	1.971 (6)[c] 2.115 (4)[d]	3.65 3.64	6.36	1.983 (4)	1.922 (5)	0.08[h]
NiL^{2+}		3.14 3.20	4.32	1.902 (9)	1.856 (10)	0.01[i]

[a] O(COH). [b] $C(O_2H)$. [c] CH_3. [d] H_2O. [e] This work. [f] Reference 8. [g] Reference 9. [h] Reference 7 [i] Reference 4b. [j] Distance of metal from N_4 plane.

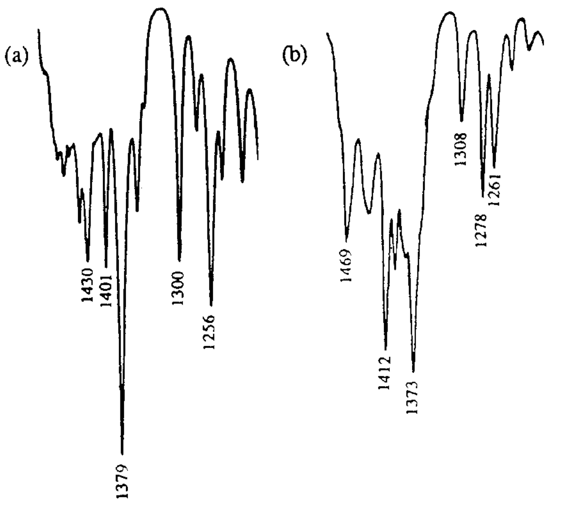

Figure 2. Infrared spectra (KBr pellets) of (a) *N-meso*-[CoL(H_2O)$_2$](ClO_4)$_2$ and (b) *N-rac*-[CoL(H_2O)](ClO_4)$_2$ in the 1500–1150-cm^{-1} region.[14]

Table VI. Electronic Absorption Spectra of *N-rac*- and *N-meso*-CoL(ClO_4)$_2$ at 22 ± 2 °C[a]

medium		λ_{max}, nm [ϵ_{max}, M^{-1} cm^{-1}]
Nujol	*N-rac*	(1650 ± 50)
	N-meso	(1550 ± 100)[b]
$(CD_3)_2CO$	*N-rac*	(1700 ± 20) [33]
	N-meso	(1700 ± 20) [12]
D_2O/H_2O	*N-rac*[c,d]	(1575 ± 10) [42], 443 [93], 327 [2415], 285 sh, 204 [14 100]
	N-meso[d,e]	(1580 ± 10) [24], 446 [120], 336 [2519], 203 [16 800]
CH_3CN	*N-rac*	(1390 ± 10) [73], 440 [120], 310 [2470], 209 [15 500]
	N-meso	(1390 ± 10) [56], 442 [138], 322 [2250], 208 [16 300]

[a] The position and intensity of a very weak band at ~750 nm[6,16] are not tabulated. [b] λ_{max} is uncertain because of the weak band intensity and the presence of water in the sample. [c] The spectrum is the same within error in 0.1 M CF_3SO_3D and 0.01 M NaOD (pD = 12.8). [d] In D_2O containing 0.1 M NaOD, λ_{max} = 1530 nm (ϵ = 44 M^{-1} cm^{-1}) and λ_{max} = 448 nm (ϵ = 88 M^{-1} cm^{-1}) is found. The species present is evidently the *N-rac* hydroxy complex. [e] In 0.1 M CD_3SO_3D.

as the primary product. On the basis of the reported[22] UV spectrum, the method of Vasilevskis and Olson also yields the meso isomer.

Equilibration. Solutions of the isomers in organic solvents or in acidic aqueous media do not equilibrate significantly even in 1 week at room temperature. Equilibration can, however, be achieved in alkaline aqueous solution. The *N-meso* to *N-rac* isomerization was studied at pH 7–12 in buffered D_2O or H_2O solutions. In all cases the "infinite-time" absorption at 1575 nm (D_2O) or 327 nm (D_2O or H_2O) was within 5% of that expected for the pure *N-rac* isomer. The spectra of comparable solutions of the *N-rac* isomer changed negligibly over the *N-meso* isomerization time scale. Thus, the *N-rac* isomer is the more stable isomer in water. The *N-rac*/*N-meso* equilibrium ratio is >10 at 25 °C; for (low-spin, four-coordinate) NiL^{2+}, the *N-rac* isomer is favored by about 6:1.[3]

The *N-meso*-CoL^{2+} isomerization rate was found to be first order in the concentration of CoL^{2+} and to increase with the alkalinity of the solution as shown in Figure 3. The interconversion rate thus conforms to the rate law $-d[N\text{-}meso\text{-}CoL^{2+}]/dt = k[OR^-][N\text{-}meso\text{-}CoL^{2+}]$, where $OR^- = OH^-$ or OD^- and $k = (5.7 \pm 1.5) \times 10^2$ M^{-1} s^{-1} at 24 ± 1 °C and pH ≥ 7. (The ionization constants 1.00×10^{-14} and 1.54×10^{-15} were used for H_2O and D_2O, respectively.[23]) The *N-meso*-/*N-rac*-CoL^{2+}

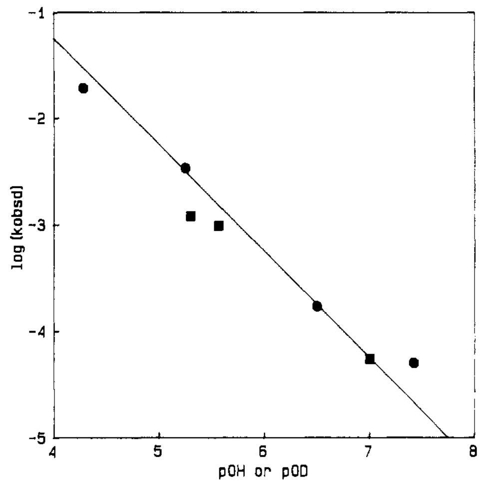

Figure 3. Dependence of *N-meso* to *N-rac* isomerization rate constants (k_{obsd}, s^{-1}) on pOD (●) or pOH (■) at 24 ± 1 °C. The line shown is that calculated for th rate law $k_{obsd} = k[OH^-$ or $OD^-]$ with $k = (5.7 \pm 1.5) \times 10^2$ M^{-1} s^{-1}. Dilute (0.4–0.8 mM) carbonate (pOD = 4.3), borate (pOD/pOH = 5.2–6.5), and phosphate (pOD/pOH = 7.0–7.4) buffers were used.

equilibration evidently proceeds via deprotonation and inversion of a secondary nitrogen (N1 or N8).[3] The experimental rate constant is thus the composite $k = K_{-H}k_{inv}$, where K_{-H} is the equilibrium constant for deprotonation of N–H by OR^- and k_{inv} is the inversion rate constant. Although few detailed studies of such processes have been reported, Sargeson's study[24] of the cobalt(III) complex $Co(en)_2(sar)^{2+}$, sar = $[O\text{–}C(O)\text{–}CH_2N\text{–}(H)(CH_3)]^-$ is noteworthy. There NH/ND exchange was found to be ~4000 times more rapid than "isomerization" (actually racemization) with both processes proceeding by a path first order in hydroxide ion. The "isomerization" rate constant was found to be 1.1×10^4 M^{-1} s^{-1} at 30 °C. The present results may also be compared with those[25] for the racemization of *N-rac*-NiL^{2+}. The NiL^{2+} racemization rate is also first order in hydroxide ion with $k = 1.4 \times 10^2$ M^{-1} s^{-1} at 25 °C.

In 0.1 M acid, the near-IR absorptions of both isomers dropped 10–20% over 10 days ($k \leq 2 \times 10^{-7}$ s^{-1}), possibly because of the reaction of CoL^{2+} with trace O_2. In any event, there was no evidence for isomerization in 0.1 M acid. In contrast, in 0.1 M OD^-, the same near-IR spectrum was obtained for both isomers, within 10 min of mixing the complexes with base. The band maximum is at 1525 nm, and its intensity suggest that the *N-rac* isomer is the major component; the shift in maximum from 1575 to 1525 (the band maximum is pH independent between pH 1 and 12) suggests the formation of a hydroxy complex. Thus, a p*K* value near 13 is implicated for water bound to *N-rac*-CoL^{2+}.[26]

The *N-meso*[5,6,9] and *N-rac* isomers are respectively six- and five-coordinate in the solid state, but the nature of their coordination environments in solution is less clear. The fact that the low-energy d–d bands shift with solvent is consistent with the presence of solvent in the primary coordination spheres of the complexes. The fact that the band maxima are the same for the two isomers in a given solvent might be taken to indicate that the coordination numbers of the two isomers are the same in solution. However, the similarity of their solid-state (d–d) spectra indicates that this is not necessarily so. Indeed, chemical evidence[21] strongly suggests that the *N-rac* isomer is present as the five-coordinate primary isomer (Figure 1, top) in acidic aqueous solution. Thus, it is possible that the solid-state structures provide an accurate reflection of the solution structures, with the species in aqueous solution being *N-meso*-$CoL(H_2O)_2^{2+}$ and *N-rac*-$CoL(H_2O)^{2+}$. Unfortunately, it does not appear that experimental techniques

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(26) Alternatively, the N1–H or N8–H group may be deprotonated rather than bound water.

available at this time can further resolve this question.

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Supplementary Material Available: Tables of crystallographic data collection parameters, thermal parameters for the non-hydrogen atoms, calculated hydrogen atom positions, bond distances and angles, and hydrogen-bonding parameters and figures showing hydrogen bonding (24 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Synthesis of (1,3-Disilylpropenyl)phosphines[1]

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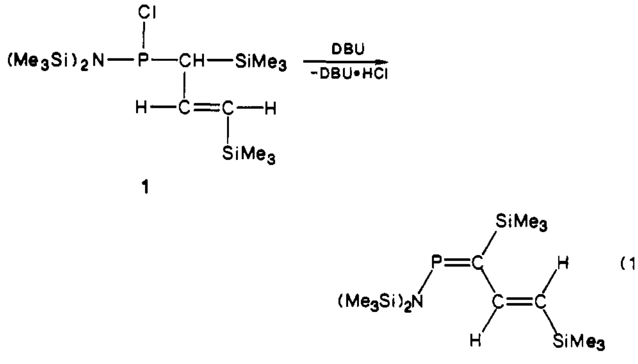
A series of the title compounds were generally prepared by the reaction of chlorophosphines RR′PCl (R, R′ = Ph, NMe_2) with [1,3-bis(trimethylsilyl)propenyl]lithium. In this manner, the new phosphine derivatives RR′P[CH($SiMe_3$)CH=CH($SiMe_3$)] (R = R′ = Ph (**3**), R = R′ = NMe_2 (**4**), R = Ph, R′ = NMe_2 (**5**)) were obtained in good yields (ca. 60–65%) as thermally stable, distillable liquids. Cleavage of the P–N bonds in **4** by treatment with anhydrous HCl gave the thermally unstable dichloro analogue, Cl_2P[CH($SiMe_3$)CH=CH($SiMe_3$)] (**6**), which did not react cleanly with *t*-BuLi to form (*t*-Bu)(Cl)P[CH($SiMe_3$)CH=CH($SiMe_3$)] (**7**). Instead, compound **7**, a distillable liquid, was obtained in good yield via the direct reaction of the disilyllithium reagent with *t*-BuPCl_2. A small amount of the disubstituted product (*t*-Bu)P[CH($SiMe_3$)CH=CH($SiMe_3$)]$_2$ (**8**) was also produced in the latter reaction. Treatment of the arylchloro(dimethylamino)phosphines, Ar(Me_2N)PCl, with (1,3-disilylpropenyl)lithium gave either the expected substitution product **9** (Ar = Mes) or a cyclic side product **10** [Ar = 2,4,6-(*t*-Bu)$_3C_6H_2$], which resulted from dehydrohalogenation of the sterically congested chlorophosphine. The series of disilylamino derivatives (Me_3Si)$_2$NP(R)[CH($SiMe_3$)CH=CH($SiMe_3$)] (R = Ph (**11**), R = Me (**12**), R = H (**13**)) were prepared either by treatment of (Me_3Si)$_2$NP(Ph)Cl with the (disilylpropenyl)lithium reagent (to give **11**) or by the reaction of the chlorophosphine (Me_3Si)$_2$NP(Cl)[CH($SiMe_3$)CH=CH($SiMe_3$)] (**1**) with organolithium compounds (with MeLi to give **12** or with *t*-BuLi to give **13**). The new compounds **3**–**13** were fully characterized by multinuclear (^{1}H, ^{13}C, ^{31}P, and ^{29}Si) NMR spectroscopy and elemental analyses.

Introduction

Recently, there has been considerable interest in the preparative, structural, and coordination chemistry of phosphadienes, the acyclic, conjugated butadiene analogues in which one or more of the carbon atoms are replaced by 2-coordinate phosphorus centers.[2] We have reported, for example, the synthesis[3] and some novel oxidation/cyclization reactions[4] of the 1-phosphadiene **2** that is kinetically stabilized by the steric bulk and π-acceptor properties of the Me_3Si groups along the P=C—C=C backbone. Compound **2** was prepared by dehydrohalogenation of the new chlorophosphine **1** (eq 1), which contained the necessary 1,3-disilylpropenyl substituent on phosphorus.

Because of their potential as precursors to phosphadienes and novel phosphorus heterocycles and as new, multidentate ligands in organometallic systems, we have conducted a more detailed investigation of the chemistry of **1** and related 1,3-disilylpropenylphosphines. Accordingly, we report here the synthesis and NMR structural characterization of a series of new phosphines that contain the 1,3-bis(trimethylsilyl)propenyl substituent.

Results and Discussion

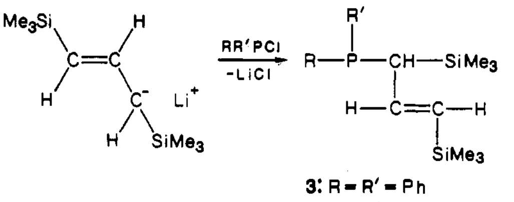


1

2

(1)

As reported for the preparation of **1**,[3] the disilylpropenyl group was introduced into the compounds described here by first preparing (1,3-disilylpropenyl)lithium by treatment of 1,3-disilylpropene with 1 equiv of *n*-BuLi and TMEDA (tetramethylethylenediamine) in Et_2O solution. Subsequent addition of 1 equiv of simple chlorophosphines afforded the corresponding (1,3-disilylpropenyl)phosphines **3**–**5** (eq 2). Compounds **3**–**5** were obtained in good yields (ca. 60–65%) as colorless, distillable liquids that were fully characterized by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy (Tables I and II) and elemental analyses (Table III).



(2)

3: R = R′ = Ph
4: R = R′ = NMe_2
5: R = Ph; R′ = NMe_2

The NMR spectroscopic data provide conclusive evidence for the assigned structures of these and the other new compounds prepared in this study. Several features are particularly noteworthy in this regard. First, as expected, the chemical shifts in the ^{31}P NMR spectra are found at ca. 80–90 ppm *upfield* from those of the starting chlorophosphines. Second, in all cases, the

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