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A Macrocyclic Tetradentate Ligand Containing Tertiary Amine and Pyridine Functional Groups. Electrochemical and X-ray Structural Studies on $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$ ($CR\text{-}Me_3$ = *meso*-2,3,7,11,12-Pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene)

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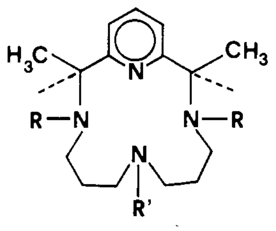
The new ligand $CR\text{-}Me_3$, *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, has been prepared by methylation of CR-H (CR-H = *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene) with formic acid and formaldehyde. The reaction of $CoCl_2$ with $CR\text{-}Me_3$ in methanol yielded $[Co^{II}(CR\text{-}Me_3)Cl]^+$, which was isolated as the perchlorate. A solution of this salt in acetonitrile yielded a reversible Co(III)/Co(II) couple at 0.69 V vs. the $Cp_2Fe^{+/0}$ couple. The high-spin (μ_{eff} = 4.8 μ_B) and air-stable $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$ complex crystallizes in space group $P2_1/n$, with a = 9.392 (2) Å, b = 17.696 (5) Å, c = 14.189 (4) Å, β = 107.36 (2)°, and Z = 4. X-ray structural analysis (R_F = 0.048 for 3316 observed Mo Kα data) showed that the macrocyclic cation conforms closely to idealized C_s molecular symmetry. The coordination geometry about the Co(II) atom is distorted tetragonal pyramidal, with one tertiary amino N atom at the apex and the metal center located 0.41 Å above the basal plane comprising the chloro ligand, the pyridyl N, and the remaining two tertiary amino N atoms.

Introduction

The design of ligands for use in the generation of strongly oxidizing inorganic complexes is a matter of current interest.[2] Macrocyclic tetradentate tertiary amines such as 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (14-TMC) have recently been found to be useful in the stabilization of high-valent strongly oxidizing ruthenium–oxo complexes.[3] However, 14-TMC and the homologues 15-TMC (1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane) and 16-TMC (1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) are very basic, so that metal-insertion reactions involving these ligands usually proceed with difficulty and result in low product yields. Mindful of extensive previous studies on the coordination chemistry of heterocyclic aromatic amines with transition-metal ions, we became interested in the title ligand $CR\text{-}Me_3$, 2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, obtainable by methylation of CR-H (CR-H = *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]hetadeca-1(17),13,15-triene).[4] First, upon complexation to a metal ion, this neutral tetradentate ligand is expected to be resistant towards oxidation. Moreover, because of the presence of the pyridyl group, it is expected to be more nucleophilic but less basic than 14-TMC and hence facilitate the metal-insertion reactions. We describe here the preparation of $CR\text{-}Me_3$, its coordination chemistry with Co(II), and the molecular geometry of the cation in $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$ as established by X-ray crystallography.



CR-H: R = R′ = H
CR-Me: R = H, R′ = CH_3
$CR\text{-}Me_3$: R = R′ = CH_3

Experimental Section

meso-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CR-H) was prepared as previously reported.[4] All reagents used were of analytical grade, and elemental analyses of the newly prepared ligand and Co(II) complex were performed by the Australian National Laboratory.

***meso*-2,3,7,11,12-Pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene ($CR\text{-}Me_3$).** A mixture of CR-H (2 g), formic acid (15 mL, 98–100%), formaldehyde (15 mL, 40%), and water (5 mL) was refluxed at 120 °C for 48 h. The reaction mixture was then transferred to a 500-mL beaker containing 50 mL of water, and the contents were cooled to ca. 5 °C in an ice–water bath. Sodium hydroxide solution was added slowly to the solution with stirring until the pH was >12. The solution was then extracted with CH_2Cl_2 (3 × 250 mL). The CH_2Cl_2 extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated down to an oily residue. This was then distilled under reduced pressure at 136–138 °C, (0.1 mmHg) to give a colorless oil. Yield: ~80%. Anal. Calcd for $C_{18}H_{32}N_4$: C, 71.4; H, 10.0; N, 18.5. Found: C, 71.3; H, 10.3; N, 18.2. Mass spectral analysis: parent molecular ion at 304. ^1H NMR in CD_2Cl_2, δ 7.61–7.44 (m), 7.06 (d), 3.62 (q), 2.33 (s), 2.26–1.9 (m), 1.42 (s), 1.34 (s). IR spectrum: no absorption at 3500–3000 cm^{-1} assignable to ν(N–H).

$[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$. $CoCl_2 \cdot 6H_2O$ (0.2 g) and $CR\text{-}Me_3$ (0.2 g) in MeOH (20 mL) were heated at ~50 °C for 10 min. Upon addition of $LiClO_4$, a dark blue precipitate was obtained. This was filtered off and recrystallized by slow diffusion of diethyl ether into an acetonirile solution of the crude product. Anal. Calcd for $CoC_{18}H_{30}N_4Cl_2O_4$: C, 43.6; H, 6.1; N, 11.3. Found: C, 43.7; H, 6.5; N, 11.6. UV-vis spectrum in CH_3CN, λ_{max}/nm ($\epsilon_{max}/M^{-1}\ cm^{-1}$): 591 (181), 557 (120), 465 (56), 250 (4650). IR spectrum (Nujol mull): pyridyl ν(C=C) and ν(C=N), 1602, 1575 cm^{-1}; no ν(H—H) stretch in the 3000–3500-cm^{-1} region.

Physical Measurements. ^1H NMR spectra were run on a JEOL FX90Q (90-MHz) spectrometer. UV-vis spectra were measured with a Beckman Acta CIII spectrophotometer. IR spectra of Nujol mulls were recorded on a Perkin-Elmer 577 spectrometer (4000–200 cm^{-1}).

Cyclic voltammetric measurements were performed by using a PAR universal programmer (Model 175), potentiostat (Model 173), and digital coulometer (Model 179). Formal potentials were taken from the mean values of the cathodic and anodic peak potentials at 25 °C at a scan rate of 100 mV s^{-1}. Cyclic voltammograms were recorded either with a Houston 2000 XY recorder at slow scan rates (<500 mV s^{-1}) or a Tektronix model 5441 storage oscilloscope at fast scan rates (>500 mV s^{-1}). All formal potential measurements were made against the $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode with ferrocene as the internal standard. Acetonitrile (Mallinkrodt Chrom A.R.) used for electrochemical studies was twice distilled over CaH_2 under argon. Supporting electrolytes were either *n*-tetrabutylammonium fluoroborate (0.1 M) or tetra-*n*-butylammonium perchlorate (0.1 M; electrometric grade, Southwestern Analytical Chemicals Inc.).

X-ray Structural Study. Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.710 69 Å), and determination of the crystal class, orientation matrix, and accurate unit cell parameters were performed according to established procedures.[5]

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Table I. Data Collection and Processing Parameters

molecular formula	[Co^{II}(CR-Me$_3$)Cl]ClO$_4$, $C_{18}H_{32}N_4O_4Cl_2Co$
M_R	498.31
cells constants	$a = 9.392$ (2) Å, $b = 17.696$ (5) Å, $c = 14.189$ (4) Å, $\beta = 107.36$ (2)°, $V = 2251$ (1) Å^3, $Z = 4$, $F(000) = 1043.8$
density (exptl)	1.472 g cm^{-3} (flotation in CCl$_4$/n-hexane)
density (calcd)	1.471 g cm^{-3}
space group	$P2_1/n$
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71069$ Å
abs coeff	10.29 cm^{-1}
cryst size	0.36 × 0.24 × 0.20 mm
mean μr	0.13
transmission factors	0.740–0.789
scan type and speed	ω–2θ; 2.02–8.37° min^{-1}
scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$
bkgd counting	stationary counts for half of the scan time at each end of scan
collcn range	$0 \leq h \leq 11, 0 \leq k < 21, \overline{17} \leq l \leq 16$; $2\theta_{max} = 52°$
no. of unique data measd	3850
no. of obsd data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	3316
no. of variables, p	277
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.048
weighting scheme	$w = [\sigma^2(F_o) + 0.0015\lvert F_o\rvert^2]^{-1}$
$R_{wF} = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.066
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.290
residual extrema in final difference map	+0.62 to −0.37 e Å^{-3}

Intensities were recorded at 22 °C, and data collection and processing parameters are summarized in Table I. The intensities were processed with the learnt-profile procedure,[6] and absorption corrections were applied by fitting a pseudoellipsoid to azimuthal scans of selected strong reflections over a range of 2θ values.[7]

Structure solution was accomplished by means of Patterson and Fourier methods. All nonhydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The hydrogen atoms of the macrocyclic ligand were generated geometrically (C–H fixed at 0.96 Å) and included in structure factor calculations with assigned isotropic thermal parameters; the methyl groups were treated as rigid groups, and the remaining hydrogen atoms were allowed to ride on their respective parent carbon atoms.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system.[8] Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[9] Blocked-cascade least-squares refinement[10] converged to the R indices and other parameters listed in Table I.

The final atomic parameters for the nonhydrogen atoms are listed in Table II, and selected bond distances, bond angles, and torsion angles are given in Table III. Other data and parameters are available as supplementary material as specified in a paragraph at the end of this paper.

Table II. Atomic Coordinates (×10^5 for Co and Cl; ×10^4 for Other Atoms) and Equivalent Isotropic Thermal Parameters[a] (Å^2 × 10^4 for Co and Cl; Å^2 × 10^3 for Other Atoms)

atom	x	y	z	U_{eq}
		[Co(CR-Me$_3$)Cl]$^+$ Cation		
Co	36908 (5)	21557 (3)	−2448 (3)	319 (2)
Cl(1)	60726 (10)	18693 (6)	7373 (7)	497 (3)
N(1)	1656 (3)	2683 (2)	−555 (2)	40 (1)
N(2)	2510 (3)	1427 (2)	494 (2)	38 (1)
N(3)	3525 (3)	1489 (2)	−1493 (2)	42 (1)
N(4)	4179 (4)	3236 (2)	−804 (2)	45 (1)
C(1)	1544 (4)	3393 (2)	−893 (3)	50 (1)
C(2)	354 (5)	3844 (3)	−842 (4)	65 (2)
C(3)	−693 (5)	3549 (3)	−445 (4)	71 (2)
C(4)	−583 (5)	2810 (3)	−128 (4)	62 (2)
C(5)	628 (4)	2379 (2)	−205 (3)	43 (1)
C(6)	867 (4)	1546 (2)	32 (3)	45 (1)
C(7)	2940 (5)	627 (2)	410 (3)	51 (2)
C(8)	2781 (5)	355 (2)	−641 (3)	51 (2)
C(9)	3843 (5)	696 (2)	−1141 (3)	52 (2)
C(10)	4739 (5)	1725 (3)	−1900 (3)	58 (2)
C(11)	4716 (6)	2539 (3)	−2235 (3)	68 (2)
C(12)	5201 (5)	3120 (3)	−1423 (4)	66 (2)
C(13)	2737 (5)	3596 (3)	−1380 (4)	61 (2)
C(14)	2812 (8)	4464 (3)	−1531 (6)	103 (3)
C(15)	−154 (5)	1194 (3)	558 (4)	69 (2)
C(16)	2962 (5)	1640 (3)	1559 (3)	55 (2)
C(17)	2082 (5)	1519 (3)	−2288 (3)	55 (2)
C(18)	4975 (6)	3704 (3)	58 (4)	69 (2)
		Perchlorate Anion		
Cl(2)	21880 (13)	−5749 (7)	28768 (9)	635 (5)
O(1)	2201 (7)	−1320 (3)	3193 (4)	138 (3)
O(2)	3579 (5)	−310 (3)	2846 (4)	121 (3)
O(3)	1221 (8)	−488 (5)	1979 (5)	250 (5)
O(4)	1759 (10)	−131 (4)	3555 (7)	209 (6)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U matrix.

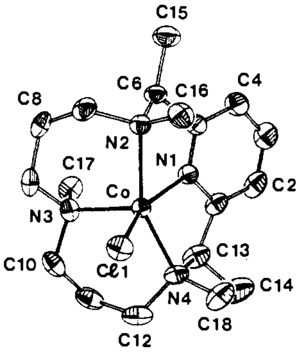

Figure 1. Molecular structure and atom numbering of the [Co^{II}(CR-Me$_3$)Cl]$^+$ cation. The thermal ellipsoids are drawn at the 35% probability level.

Results and Discussion

The CR-Me$_3$ ligand was prepared by N-methylation of CR-H in a manner similar to that employed for 14-TMC.[11] Unlike CR-H, which is a crystalline solid, CR-Me$_3$ is a nearly colorless viscous oil at room temperature, and this is probably due to its reduced capability for intermolecular hydrogen bonding.

The Co(II) complex of CR-Me$_3$ forms readily in methanolic solution to give [Co^{II}(CR-Me$_3$)Cl][ClO$_4$] as a deep blue solid. Magnetic susceptibility measurements confirm an oxidation state of +2 and indicate a pentacoordinate high-spin electronic configuration. The measured magnetic moment of 4.8 μ_B is comparable to the corresponding values for [Co^{II}(14-TMC)(H$_2$O)]$^{2+}$ (4.45 μ_B)[12] and [Co(Et$_4$dien)Cl$_2$] (4.71 μ_B).[13,14] As in the

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Table III. Bond Lengths (Å), Selected Bond Angles (deg), and Torsion Angles (deg) in the $[Co^{II}(CR\text{-}Me_3)Cl]^+$ Cation

Co–Cl(1)	2.311 (1)	N(3)–C(17)	1.483 (5)	N(4)–C(13)	1.499 (5)	N(2)–C(6)	1.501 (5)
Co–N(1)	2.053 (3)	Co–N(3)	2.095 (3)	N(4)–C(12)	1.497 (7)	N(2)–C(7)	1.485 (5)
Co–N(2)	2.164 (3)	Co–N(4)	2.171 (4)	C(11)–C(12)	1.509 (7)	C(7)–C(8)	1.532 (6)
N(1)–C(1)	1.338 (5)	N(1)–C(5)	1.325 (5)	C(10)–C(11)	1.515 (8)	C(8)–C(9)	1.512 (7)
C(1)–C(2)	1.393 (7)	C(4)–C(5)	1.401 (6)	N(3)–C(10)	1.483 (6)	N(3)–C(9)	1.490 (5)
C(2)–C(3)	1.373 (8)	C(3)–C(4)	1.378 (7)	C(13)–C(14)	1.555 (7)	C(6)–C(15)	1.514 (8)
C(1)–C(13)	1.523 (7)	C(5)–C(6)	1.513 (6)	N(4)–C(18)	1.480 (6)	N(2)–C(16)	1.491 (5)
N(3)–Co–Cl(1)	101.6 (1)	N(3)–Co–N(1)	104.2 (1)	C(2)–C(1)–C(13)	126.8 (4)	C(4)–C(5)–C(6)	125.6 (4)
N(3)–Co–N(2)	98.9 (1)	N(3)–Co–N(4)	99.9 (1)	C(1)–C(13)–N(4)	108.7 (4)	C(5)–C(6)–N(2)	107.4 (3)
Cl(1)–Co–N(2)	96.9 (1)	Cl(1)–Co–N(4)	98.1 (1)	C(13)–N(4)–C(12)	111.8 (3)	C(6)–N(2)–C(7)	111.6 (3)
N(1)–Co–N(2)	78.3 (1)	N(1)–Co–N(4)	78.8 (1)	N(4)–C(12)–C(11)	116.2 (4)	N(2)–C(7)–C(8)	115.3 (3)
C(1)–N(1)–C(5)	121.9 (4)	C(2)–C(3)–C(4)	120.1 (5)	C(12)–C(11)–C(10)	115.8 (4)	C(7)–C(8)–C(9)	116.5 (3)
N(1)–C(1)–C(2)	119.8 (4)	N(1)–C(5)–C(4)	120.5 (4)	C(11)–C(10)–N(3)	116.7 (4)	C(8)–C(9)–N(3)	116.0 (4)
C(1)–C(2)–C(3)	119.2 (4)	C(3)–C(4)–C(5)	118.3 (5)	C(10)–N(3)–C(9)	107.2 (3)		
N(1)–C(1)–C(13)	113.2 (4)	N(1)–C(5)–C(6)	113.7 (3)				

N(1)–C(1)–C(13)–N(4)	−38.5 (5)	N(1)–C(5)–C(6)–N(2)	40.0 (5)
C(1)–C(13)–N(4)–C(12)	155.7 (4)	C(5)–C(6)–N(2)–C(7)	−158.5 (4)
C(13)–N(4)–C(12)–C(11)	−68.2 (5)	C(6)–N(2)–C(7)–C(8)	67.1 (5)
N(4)–C(12)–C(11)–C(10)	−68.7 (6)	N(2)–C(7)–C(8)–C(9)	68.3 (5)
C(12)–C(11)–C(10)–N(3)	75.0 (5)	C(7)–C(8)–C(9)–N(3)	−74.6 (4)
C(11)–C(10)–N(3)–C(9)	−175.5 (3)	C(8)–C(9)–N(3)–C(10)	176.6 (3)
C(11)–C(10)–N(3)–C(17)	65.9 (4)	C(8)–C(9)–N(3)–C(17)	−65.1 (4)
N(1)–C(1)–C(13)–C(14)	−166.3 (4)	N(1)–C(5)–C(6)–C(15)	172.3 (3)
C(1)–C(13)–N(4)–C(18)	−83.5 (4)	C(5)–C(6)–N(2)–C(16)	80.5 (4)
C(14)–C(13)–N(4)–C(18)	42.3 (6)	C(15)–C(6)–N(2)–C(16)	−51.5 (5)

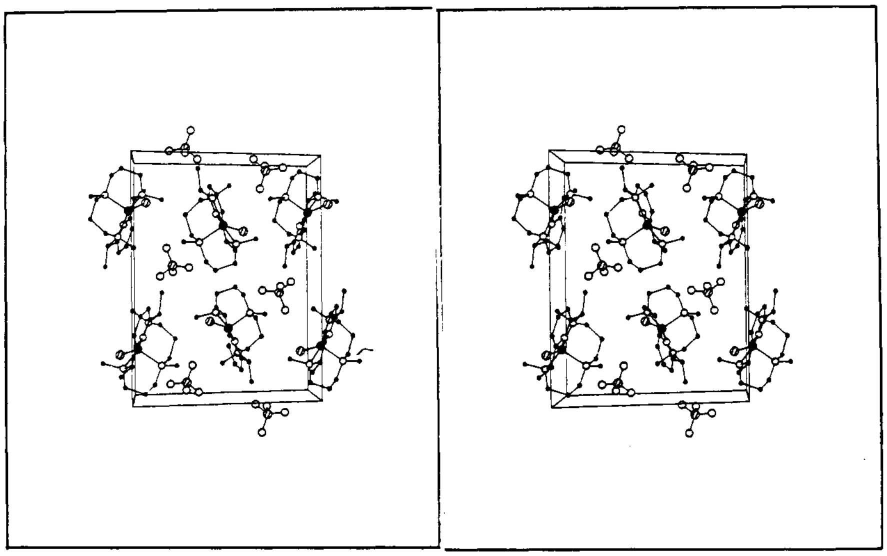

Figure 2. Steroview of the molecular packing in $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$. The origin of the unit cell lies at the upper left corner, with *a* pointing toward the reader, *b* downward, and *c* from left to right.

high-spin trigonal-bipyramidal $[Co(Et_4dien)Cl_2]$ case, the three UV–vis bands at 591, 557, and 465 nm of $[Co^{II}(CR\text{-}Me_3)Cl]^+$ are due to the spin-allowed d–d transitions. The infrared absorption spectrum of $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$ displays a doublet in the 1570–1610-cm^{-1} region assignable to the ν(C=C) and ν(C=N) stretches of the pyridine ring.

The structure and atomic numbering scheme of the $[Co^{II}(CR\text{-}Me_3)Cl]^+$ cation is illustrated in Figure 1, and the molecular packing, in Figure 2. The perchlorate anion is well ordered. The macrocyclic cation conforms closely to idealized C_s molecular symmetry. The coordination geometry about the Co(II) atom is distorted tetragonal pyramidal, with one tertiary amino N(3) atom at the apex and the metal center located 0.41 Å above the basal plane comprising the chloro ligand, the pyridyl N(1) atom, and the remaining two tertiary amino N atoms [N(2) and N(4)]. The CR-Me$_3$ ligand is thus in a folded configuration, the N(3)–Co–N(1) angle being 98.9 (1)°. Indeed, a similar cis coordination mode of a related pyridyl macrocycle, CR-Me (2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1-(17),13,15-triene), has recently been reported.[15] In accord with

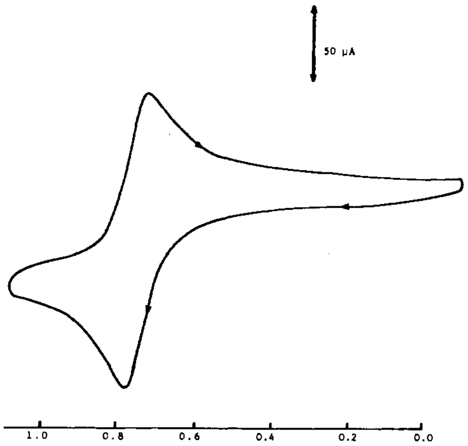

Figure 3. Cyclic voltammogram of $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$ (1 mM) in 0.1 M $[Bu_4N]BF_4$ acetonitrile solution: working electrode, pyrolytic graphite; scan rate, 20 mV s^{-1}. The potentials (in V) are referenced vs. Ag/AgNO$_3$ (0.1 M in CH$_3$CN).

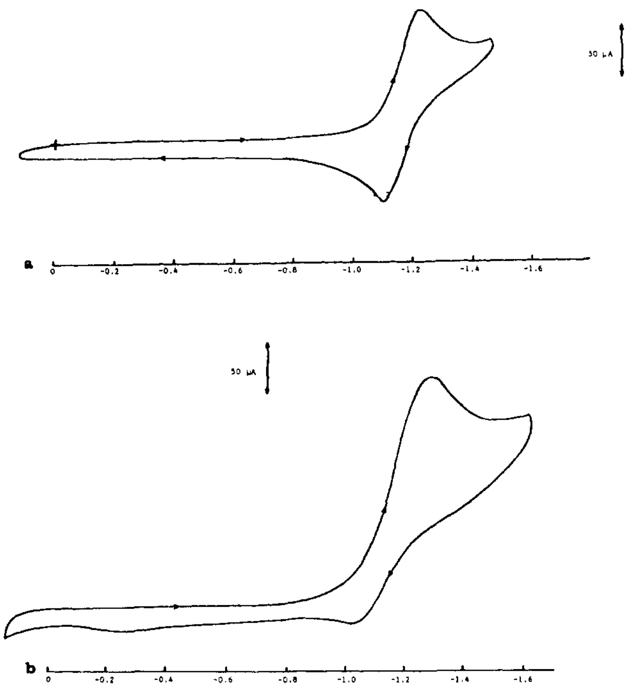

Figure 4. Cyclic voltammogram of O_2 (saturated in 0.1 M $[Bu_4N]BF_4$ acetonitrile solution) in (a) the absence and (b) the presence of $[Co^{II}(CR\text{-}Me_3)Cl]^+$ (1 mM): working electrode, pyrolytic graphite; scan rate, 100 mV s^{-1}. The potentials (in V) are referenced vs. $Ag/AgNO_3$ (0.1 M in CH_3CN).

the meso isomer formulation for the present complex, the two C–CH_3 groups, C(14) and C(15), lie above the mean plane comprising the pyridine ring and atoms C(6) and C(13). The three N–CH_3 groups [C(16), C(17), and C(18)] adopt the "two up and one down" configuration with the Co–Cl and N(3)–C(17) bonds trans to each other. The N(3)–Co–N(1) and N(3–)Co–Cl(1) bond angles, 104.2 (1) and 101.6 (1)° respectively, are much smaller than N(1)–Co–Cl(1) [154.2 (1)°], possibly as a consequence of the nonbonded steric interactions between the N–CH_3, Co–Cl, and C–CH_3 groups. The Co–Cl and Co–N(tertiary amine) bond distances are comparable to the corresponding values in $[Co(Et_4dien)Cl_2]$.[14]

It is generally known that macrocyclic tertiary amines are capable of imposing five-coordination on transition-metal ions.[16] We believe that the unusual geometry of the Co(II)–macrocyclic tertiary amine complexes is responsible for their stabilities toward aerobic oxidation.[12] Figure 3 shows the cyclic voltammogram of $[Co^{II}(CR\text{-}Me_3)Cl]^+$ in acetonitrile. A quasi-reversible one-electron redox couple [$\Delta E_p \sim$ 70–80 mV, scan rate = 100 mV s^{-1}, i_{pa}/i_{pc} = 1), attributed to the oxidation of Co(II) to Co(III), was observed at a potential of 0.69 V vs. the $Cp_2Fe^{+/0}$ couple. The *remarkably high oxidation potential of* $[Co^{III}(CR\text{-}Me_3)Cl]^{2+}$ *is unexpected* since the $E_{1/2}$ value of the analogous $[Co^{III}(14aneN_4)(H_2O)_2]^{3+}/[Co^{II}(14aneN_4)(H_2O)_2]^{2+}$ couple (14aneN_4 = 1,4,8,11-tetraazacyclotetradecane) is only 0.16 V vs. SSCE.[17] The instability of five-coordinate Co(III) species is understandable since Co(III) complexes are usually six-coordinate. Figure 4 illustrates the cyclic voltammograms for the electrochemical reduction of O_2 to O_2^- in acetonitrile. In the absence of $[Co^{II}(CR\text{-}Me_3)Cl]^+$, a quasi-reversible O_2/O_2^- couple was found at −1.16 V vs. the $Cp_2Fe^{+/0}$ couple. In the presence of the Co(II) complex, the reduction of O_2 to O_2^- became irreversible, only a reductive wave at ~−1.3 V being observed. In this potential range, Co(II) is electrochemically inactive and hence oxidation of O_2^- by Co(II) through an outer-sphere pathway is not feasible. Thus it may be argued that the irreversible electrochemical behavior is possibly due to the removal of the electrochemically generated O_2^- through binding with $[Co^{II}(CR\text{-}Me_3)Cl]^+$. The exact nature of the reaction mechanism is presently under investigation, but the five-coordinate nature of Co(II)–tertiary amine complexes does provide a vacant coordination site for interaction with small molecules, which is undoubtedly an important factor in catalysis. Recent studies have shown that Os, Ru, Ni, and Cu complexes of CR-Me_3 can be prepared in high yield,[18] the details of which will be reported later.

Registry No. CR-H, 22730-78-5; CR-Me_3, 105103-66-0; $[Co^{II}(CR\text{-}Me_3)Cl]ClO_4$, 105103-68-2; formaldehyde, 50-00-0; formic acid, 64-18-6; O_2, 7782-44-7.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic temperature factors, and additional bond distances and bond angles (3 pages); a table of structure factors (20 pages). Ordering information is given on any current masthead page.

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