zation, occurring within the solvent cage, can be visualized. This involves a lithium atom behaving as a pivotal point about which the halogen can migrate from one side to the other. This is also the case when both the lithium and halogen have to produce a carbene. Reaction of *tert*-butyllithium with these species leads to racemic **5**. The net result is overall inversion of configuration. The process is reminiscent of solvolysis reactions involving chiral substrates. Although vinyl halides ionize with extreme difficulty, carbenoids (metal-substituted vinyl halides) appear to ionize more readily. We refer to this as ***metal-assisted ionization***. The mechanism can also be applied to the Fritsch–Buttenburg–Wiechell rearrangement in which it has been shown that the migrating group has a trans relationship with the leaving group.[18]

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Registry No. (a*S*)-(+)-**1**, 60164-94-5; (a*S*)-(−)-**4**-*d*, 91296-37-6; (a*R*)-(−)-**5**-*d*, 91296-38-7; (a*S*)-(+)-**5**, 91296-39-8; (a*S*)-(−)-**6**-*d* (isomer 1), 91383-55-0; *t*-BuLi, 594-19-4; $(t\text{-Bu})_2CuLi$, 23402-75-7; (a*S*)-(−)-**6**-*d* (isomer 2), 91296-40-1.

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Synthesis and Characterization of Stable Cobalt(IV) Coordination Complexes: Molecular Structure of *trans*-[η^4-1,2-Bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene]bis(4-*tert*-butylpyridine)cobalt(IV)

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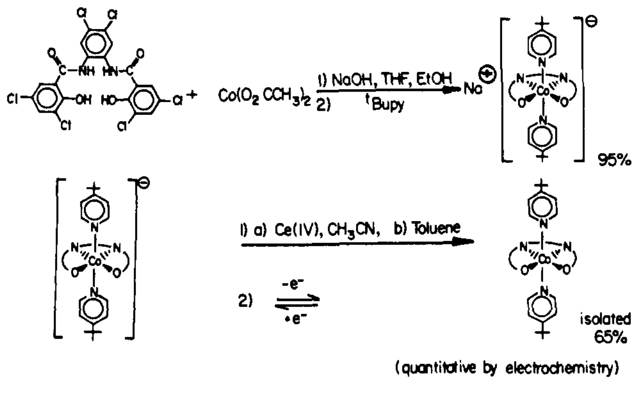
We are interested in contributing to oxidation chemistry by preparing coordination complexes with transition metals in unusual, high oxidation states for use as oxidizing agents. Our approach has been to employ multianionic chelating ligands that have been designed to be compatible with highly oxidized metal centers and the media necessary to generate them.[2] Here we report the synthesis of stable complexes of Co(IV) and their characterization by spectroscopic and single-crystal X-ray diffraction methods. With the exception of several homoleptic halide and oxide complexes,[3] this work contains the first structural study of a Co(IV) coordination complex.[4] The oxidative electrochemistry of a number of cobalt coordination compounds has been previously investigated.[5] Organocobalt(IV) complexes have been detected by cyclic voltammetry.[6] In addition, several of these complexes have been generated at low temperature and characterized by EPR spectroscopy.[7]

Scheme I



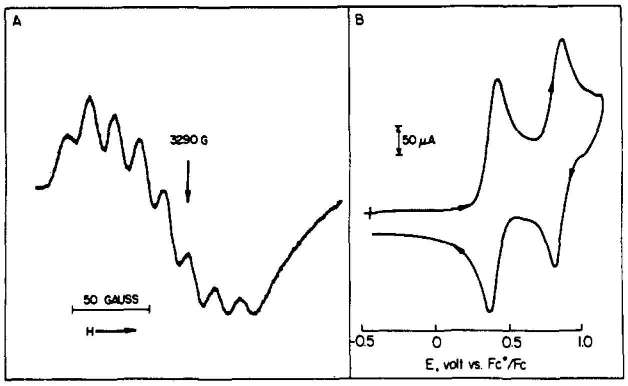


Figure 1. A: First derivative EPR spectrum of *trans*-Co(η^4-CHBA-DCB)(t-Bupy)$_2$ in frozen toluene at 10 K. Microwave frequency is 9.198 MHz. B: Cyclic voltammogram of 3.7 mM Na[*trans*-Co(η^4-CHBA-DCB)(t-Bupy)$_2$]·H_2O in CH_3CN, 0.1 M TBAP at 0.174-cm^2 BPG electrode. Scan rate = 200 mV/s^{-1}.[11]

Treatment of $Co(O_2CCH_3)_2$ with 1 equiv of H_4(CHBA-DCB)[2,8] in THF/EtOH followed by addition of excess NaOH and 4-*tert*-butylpyridine (*t*-Bupy) yields a deep red solution after stirring for 0.5 h at room temperature (Scheme I). The complex Na[*trans*-Co(η^4-CHBA-DCB)(t-Bupy)$_2$]·H_2O was isolated in 95% yield by removal of excess *t*-Bupy under vacuum and filtration through silica gel in THF. The solid obtained by evaporation of the THF solution was recrystallized from CH_2Cl_2/hexane.[9] Oxidation of Na[*trans*-Co(η^4-CHBA-DCB)(t-Bupy)$_2$]·H_2O with 1 equiv of ceric ammonium nitrate in CH_3CN affords *trans*-Co(η^4-CHBA-DCB)(t-Bupy)$_2$ in 65% isolated yield by removal of CH_3CN under vacuum and extraction into, and crystallization from, toluene.[10]

The dark green complex was characterized by its EPR spectrum in frozen toluene solution at 10 K (Figure 1A), which shows the eight-line pattern expected for a Co ($I = {}^7/_2$) centered radical at $g = 2.011$ with Co hyperfine splitting of 1.5×10^{-3} cm^{-1} (16 G). The *g* value is similar to and the isotropic hyperfine coupling slightly larger than those reported for organobis(dioximato)co-

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[8] Abbreviations: H_4(CHBA-DCB), 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene; H_4(CHBA-Et), 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane; *t*-Bupy, 4-*tert*-butylpyridine; py, pyridine; THF, tetrahydrofuran; Et, ethyl; SCE, saturated calomel electrode; BPG, basal plane pyrolytic graphite; TBAP, tetrabutylammonium perchlorate; DMAP, 4-dimethylaminopyridine; Fc, ferrocene.

[9] ^1H NMR spectroscopic data: $((CD_3)_2CO)$ δ 9.38 (s 2 H), 8.22 (d, $J = 6$ Hz, 4 H), 7.83 (d, $J = 3$ Hz, 2 H), 7.22 (d, $J = 6$ Hz, 4 H), 7.13 (d, $J = 3$ Hz, 2 H), 3.04 (s, (H_2O, 2 H), 1.16 (s, 18 H). Anal. Calcd for $C_{38}H_{34}Cl_6CoN_4NaO_5$: C, 49.54; H, 3.72; N, 6.08. Found: C, 49.28; H, 3.78; N, 6.16.

[10] Anal. Calcd for $C_{38}H_{32}Cl_6CoN_4O_4$: C, 51.84; H, 3.66; N, 6.36. Found: C, 51.51; H, 3.83; N, 6.08.

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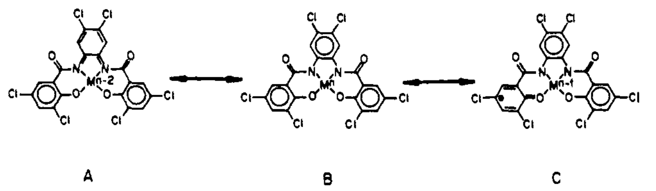
Scheme II



balt(IV) complexes.[7] Nitrogen superhyperfine coupling is not observed. The electronic spectrum in toluene exhibits absorbances at 369 ($\epsilon = 1.23 \times 10^4$ M^{-1} cm^{-1}), 419 ($\epsilon = 6.38 \times 10^3$ M^{-1} cm^{-1}), 444 ($\epsilon = 4.81 \times 10^3$ M^{-1} cm^{-1}), and 668 nm ($\epsilon = 2.27 \times 10^3$ M^{-1} cm^{-1}); the latter three bands are not present in the Co(III) complex. Variable-temperature magnetic susceptibility measurements over the temperature range 5–300 K follow Curie–Weiss behavior with a magnetic moment of 1.75 μ_B at 298 K.

Cyclic voltammetry of Na[*trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$]·H$_2$O shows a reversible Co$^{IV/III}$ couple at $E_f = +0.39$ V vs. Fc$^+$/Fc and a second reversible one-electron couple at +0.84 V (Figure 1B).[11] Electrolytic oxidation in CH$_3$CN or CH$_2$Cl$_2$ at +0.60 V consistently consumed 1.05–1.10 *F*/mol Co(III). We believe this value exceeds 1.0 because the second oxidation also proceeds to a small extent at +0.60 V. The electrochemically generated Co(IV) complexes are identical in all respects with those prepared by ceric ion oxidation. We are currently studying the second oxidation product and related more oxidized materials. The potentials of the reversible couples are dependent on the nature of both the axial base and the chelating ligand. Thus, the Co$^{IV/III}$ potential is shifted to +0.23 V when the chlorine atoms on the benzamide bridge are replaced by hydrogen atoms. Similarly, Na[trans-Co(η^4-CHBA-DCB)(DMAP)$_2$]·H$_2$O,[12] with a different pair of axial ligands, is oxidized to the corresponding Co(IV) complex[13] at +0.33 V.

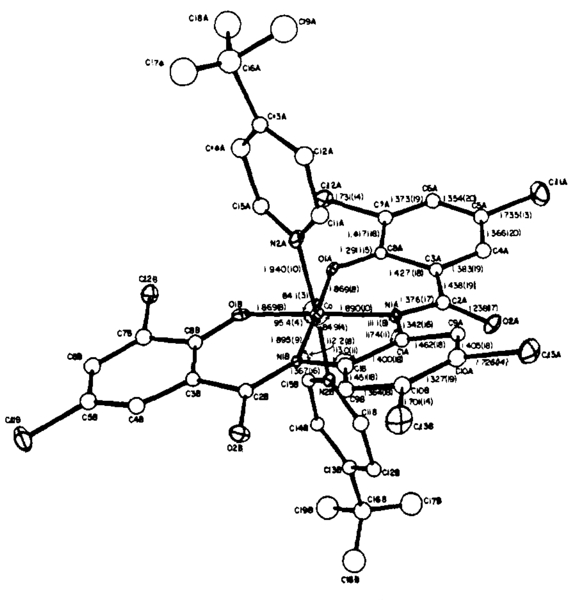


Figure 2. ORTEP representation of *trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$.

The molecular structure of *trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$ has been determined by X-ray crystallography (Figure 2).[14] It is important to note that in addition to the tetradentate tetraanion formulation B for the chelating ligand, structures such as the benzoquinone diimine A or phenoxoid radical C are also plausible (Scheme II). These structures alter the formal oxidation state assignment at the metal. The structural data do not reveal systematic distortions that would signal an overwhelming importance of the alternative structures when comparisons are made with X-ray studies of N-bound Copper(II) {1,2-bis(2-picolinamido)-benzene}[15] and Co^{II}- and Co^{III}(salen)[16] complexes where these structures are unlikely. We believe that the tetradentate tetraanion formulation is the most appropriate description and that Co(IV) is readily accessible in this ligand environment principally because the ligand is an exceptionally powerful donor *because of the bonding properties of the coordinating atoms*. Enhancement of the donor ability by the extended π-system of the planar ligand is probably of secondary importance. The ability of N-coordinated secondary organic amido ligands to significantly reduce formal reduction potentials is well documented in compounds where such π-delocalization effects are absent.[17] It should be noted that, in the analogous Os(IV) system,[2] replacement of the dichlorophenylene unit of the tetradentate ligand in Os(η^4-CHBA-DCB)(py)$_2$ with the ethylene unit in Os(η^4-CHBA-Et)(py)$_2$ results in a negligible increase (0.82 → 0.86 V) of the reversible potential for the first oxidation step.[18] If the benzoquinone diimine (or semibenzoquinone diimine) form of the dichlorophenylenediamide moiety was important, it would be expected that the formal potential would occur at a significantly more positive value for the ethylene-containing ligand relative to the dichlorophenylene-containing ligand. The free base ligand H$_4$(CHBA-DCB) is oxidized, albeit irreversibly, at a more positive potential (0.60 V)[19] than that of the Co$^{IV/III}$ couples reported herein.

The isolation and structural characterization of stable coordination compounds of Co(IV) illustrates the ability of oxidation-resistant, multianionic, chelating ligands to stabilize rare oxidation states. We are continuing to exploit this property with a number of metals.

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Supplementary Material Available: Listings of bond distances and angles (Table I), fractional atomic coordinates and Gaussian amplitudes (Table II), and structure factor amplitudes (Table III) (22 pages). Ordering information is given on any current masthead page.

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(11) Reported potentials are referenced to ferrocene, Fc$^+$/Fc, as an internal standard. We find the Fc$^+$/Fc potential to be +0.39 V vs. aqueous SCE. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peak potentials.

(12) ^{1}H NMR spectroscopic data ((CD$_3$)$_2$CO): δ 9.30 (s, 2 H), 7.91 (d, (J = 3 Hz, 2 H), 7.64 (d, J = 7 Hz, 4 H); 7.17 (d, J = 3 Hz, 2 H), 6.31 (d, J = 7 Hz, 4 H), 3.04 (s, H$_2$O, 2 H), 2.87 (s, 12 H).

(13) EPR spectroscopic data (CH$_2$Cl$_2$, 298 K): $g = 1.998$; $a = 1.3 \times 10^{-3}$ cm^{-1} (14 G). FAB-MS (8 kV), *m/e* 851.

(14) Crystal data: space group P2$_1$/*c*,a = 11.73 (5) Å, b = 24.22 (7) Å, c = 13.90 (2) Å, β = 100.8 (1)°, V = 3879 (6) Å^3, Z = 4. Data were collected on a locally modified Syntex p2$_1$ diffractometer with graphite monochromator and Mo Kα radiation (λ = 0.71069 Å) to $2\theta = 40°$ ($\pm h$, $\pm k$, $\pm l$). The averaged data (3648) were corrected for Lorentz, polarization, and absorption effects (μ = 9.109 cm^{-1}). The Co atom position was derived from the Patterson map, and subsequent difference Fourier maps revealed the remaining non-hydrogen atoms. Least-squares refinement of atomic coordinates and B's, minimizing $\sum w[F_0^2 - (F_c/k)^2]^2$ with weights $w = [\sigma^2(F^2) + (0.02 \times \text{scan counts})^2]^{-1}$, gave $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.23$ (2894 reflections with $F_o^2 > 0$). Hydrogen atoms were introduced into calculated positions with B = 12 Å^2 for methyl hydrogen atoms and B = 5 Å^2 for all other hydrogen atoms. Refinement of carbon atoms with isotropic Gaussian amplitudes and the remaining non-hydrogen atoms with anisotropic Gaussian amplitudes resulted in $R_F = 0.075$ for the 2004 reflections with $F_o^2 > 3\sigma(F^2)$ and GOF = 2.53.

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(19) Measured in 10:1 acetonitrile/dimethylformamide.