therefore, it will find further applications for selective carbon–carbon bond formation.

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(2) Although a large part of the chromic chloride apparently is undissolved, a small portion of the salt seemingly dissolved. To this the spontaneous hydrogen evolution can be ascribed.

(3) In another experiment [$LiAlH_4$ (1.2 mmol), $CrCl_3$ (2.4 mmol) in THF (2 mL), PhCHO (1 mmol), and prenyl bromide (1.2 mmol)] 90% yield was estimated by GLC assay.

(4) Similar allyl transposition is observed in the reaction of allyllithium and allylmagnesium halide: (a) T. E. Stanberry, M. J. Darmon, H. A. Fry, and R. S. Lenox, *J. Org. Chem.*, **41**, 2052 (1976); (b) F. Barbot and P. Miginiac, *Tetrahedron Lett.*, 3829 (1975), but allylzinc halide gives a mixture of regioisomers.

(5) Homocoupling of allylic and benzylic halides will be published elsewhere.

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(8) M. Gaudemar, *Tetrahedron*, **32**, 1689 (1976).

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(10) A large-scale synthesis of artemisia alcohol: chromic chloride (4.28 g, 27 mmol) was reduced with lithium aluminum hydride (513 mg, 13.5 mmol) in THF (20 mL). After stirring at room temperature for 10 min, 3-methyl-2-butenal (0.56 g, 6.1 mmol) and subsequently prenyl bromide (2.01 g, 13.5 mmol) in THF (10 mL) were added dropwise during the period of 20 min. Stirring for 3 h, followed by workup and distillation (97–100 °C (4 mm), Kugelrohr), gave an oil (0.90 g, 88% yield) consistent with artemisia alcohol spectrometrically.

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Yoshitaka Okude, Shigeo Hirano
Tamejiro Hiyama,* Hitosi Nozaki

Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

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Sepulchrate: A Macrobicyclic Nitrogen Cage for Metal Ions

Sir:

Ligands which effectively encapsulate metal ions inhibit ligand substitution but offer interesting prospects for the study of intramolecular rearrangements, electron transfer, and spectroscopic properties. The ligands classified as cryptates[1] are in this category and this note describes a structure and some chemistry of cobalt complexes of an octaazacryptate ligand synthesized on the metal by condensing the tris(ethylenediamine)cobalt(III) ion with formaldehyde and ammonia, (yield >95%).

The complex (*S*)-[(1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane)cobalt(III)]$^{3+}$ has been given the trivial name [Co(sepulchrate)]$^{3+}$ in keeping with the cryptate nomenclature. The crystal structure (Figure 1) confirms that synthesis occurs with retention of the chirality of the $Co(en)_3{}^{3+}$ ion and shows the sexadentate nature of the capsule with the tris(methylene) amino cap added at both ends of the parent ion. The ethylenediamine rings have the *lel* conformation and the overall symmetry is very close to D_3. Quantitative conformational analysis calculations[2] were done for this unexpected conformation and two others indicated by Dreiding models: a C_3 *lel* and a D_3 *ob*. The C_3 conformer has catoptric caps and the D_3 conformers have caps of the same chirality. The strain energy differences of the conformers are 1.4, 1.4, and 0 kcal/mol, respectively. The calculations indicate that the conformer found in the crystal is not the most stable and most likely it is stabilized by hydrogen bonding to lattice Cl^- ions. The ^{1}H and ^{13}C NMR spectra indicate D_3 symmetry for the ion in solution or rapid interconversion of the conformers ($\{^{59}Co\}$ ^{1}H signals at δ 4.0 ppm, 12 protons, AB doublet pair, $J \sim 12$ Hz; $\delta \sim 3.2$ ppm, complex AA′BB′ pattern, 12 protons, relative to external tetramethylsilane for the N-deuterated complex; ^{13}C spectrum shows two signals of equal intensity at $\delta - 0.389$ ppm and $\delta + 13.245$ ppm relative to 1,4-dioxane). The low field proton signals are assigned to the methylene caps and the complex pattern to the ethylenediamine residues.

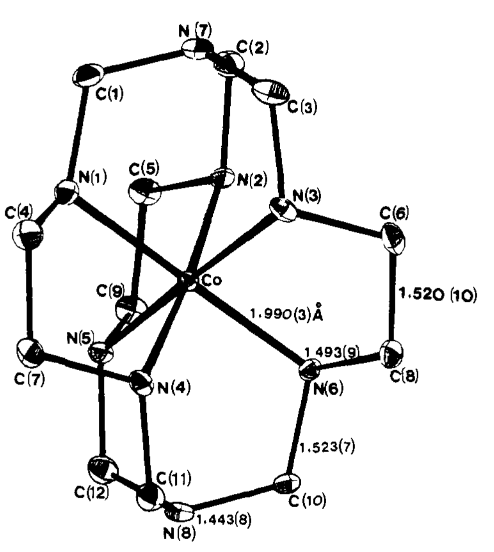

Figure 1. ORTEP diagram of Co(sepulchrate)$^{3+}$ with 20% thermal ellipsoids. Not shown are hydrogen atoms and hydrogen bonding of chlorides to cis pairs of NH groups. (The trichloride monohydrate salt crystallizes in space group $P2_12_12_1$ with $a = 15.60$ (1), $b = 14.868$ (7), and $c = 8.757$ (4) Å and $Z = 4$.) X-ray data (3166 reflections) were collected by diffractometer with monochromatic Mo Kα radiation. Anisotropic full-matrix least-squares refinement (hydrogen atoms isotropic at calculated positions) on F converged to a final $R = 0.038$.

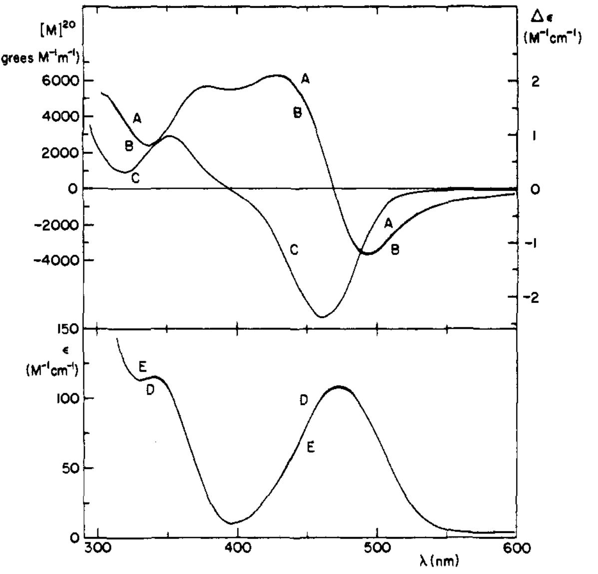

Figure 2. Rotatory dispersion (A, 0.1 M HCl), circular dichroism (C, H_2O), and visible absorption spectra (D, 0.1 M HCl) of (*S*)-[Co(sep)]$Cl_3 \cdot H_2O$. Curves B and E were obtained by oxidizing the Co(II) salt and measuring the solutions under the same conditions as A and D.

Cyclic voltammetry (100 mV/s in 0.1 M $NaClO_4$, 25 °C) showed an essentially reversible reduction wave at −0.54 V vs. the saturated calomel electrode (70 mV peak to peak, i_{pf}/i_{pb} 1.0, E^0 −0.30 V). The reduction potential is lower than that observed for $Co(en)_3{}^{2+/3+}$ (−0.45 V, irreversible) under the same conditions. E^0 for $Co(en)_3{}^{2+/3+}$ is −0.259 (1 M KCl).[3] Using Zn dust in excess the reduction to Co(II) occurs within seconds for $[H^+] = 10^{-2}$ to 10^{-7} M and the Co(II) salt was isolated as the $ZnCl_4{}^{2-}$ salt. The Co(II) ion reoxidizes with

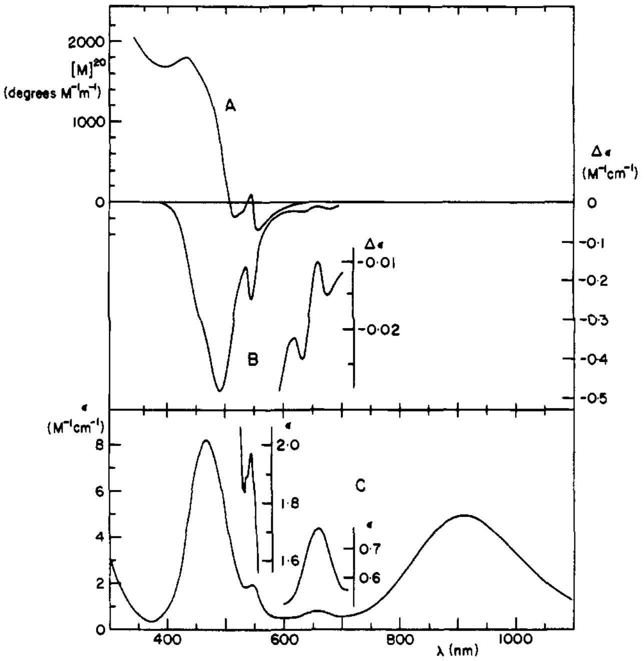

Figure 3. Rotatory dispersion (A), circular dichroism (B), and visible absorption spectra (C) of aqueous solutions of (S)-$[Co(sep)]^{2+}$ obtained by reducing (S)-$[Co(sep)]Cl_3 \cdot H_2O$ in water with Zn (dust).

O_2 quantitatively to the Co(III) ion and H_2O_2 with retention of absolute configuration (>99%). The oxidation of $[Co^{II}(sep)]^{2+}$ by O_2 was followed spectrophotometrically over the range $0.1 \geqslant [H^+] \geqslant 10^{-3}$ at $\mu = 0.2$ M (NaCl, HCl) and 25 °C. For pseudo-first-order conditions with excess O_2 and Co(II) a rate law of the form, $-\mathrm{d}[O_2]/\mathrm{d}t = -\frac{1}{2}\mathrm{d}[(Co(sep)^{2+}]/\mathrm{d}t = k_{ox}[Co(sep)^{2+}][O_2]$ was obtained, where $k_{ox} = 44 \pm 5$ M^{-1} s^{-1}. The addition of O_2 to the Co(II) ion appears improbable because of the ligand insulation but attempts to detect the superoxide ion by rapid flow and EPR techniques were unsuccessful.[4]

The visible spectra for both oxidation states are given in Figures 2 and 3 along with their circular dichroism and rotatory dispersion curves. The symmetry requires all the chiral N atoms to have the same configuration (S) for the structure derived from $\Lambda[Co(en)_3]^{3+}$. The CD curves for the Co(III) ions around 500 nm for these two entities are essentially catoptric despite the origin of the sexadentate. This result is predicted by calculations based on the optical activity models of Richardson for both the C_3 and D_3 conformers.[5]

Interesting aspects of these results are the spectroscopic properties, the retention of chirality in the Co(II) ions, the quantitative oxidation of $[Co^{II}sep]^{2+}$ to $[Co^{III}sep]^{3+}$ without the formation of a peroxy-bridged dimer and the (essentially) reversible redox phenomena. The retention of chirality implies no loss of Co^{2+} ion from the ligand and this was confirmed using ${}^{60}Co_{aq}{}^{2+}$ as a tracer. Less than 1% exchange was observed in 24 h.

The electron transfer rate was measured by mixing (R)-$(+)_{490}$-$Co(sep)^{3+}$ and (S)-$(+)_{490}$-$Co(sep)^{2+}$. For equal concentrations of the two ions electron transfer leads to racemization and the electron transfer rate was followed by the change in optical rotation (α) at 500 nm. The data yield a rate law of the form $-\mathrm{d}\ln(\alpha - \alpha_\infty)/\mathrm{d}t = k_{et}[Co]_{total} = k_{obsd}$ where $k_{et} = 5.1 \pm 0.3$ M^{-1} s^{-1} ($\mu = 0.2$ M (NaCl, HCl); H^+, 10^{-7} to 10^{-2} M; 25 °C). The rate constant is $\sim 10^5$-fold greater than that for $Co(en)_3{}^{2+/3+}$ (at 25 °C, $k = 7.7 \times 10^{-5}$ M^{-1} s^{-1} measured by the same method[6] or $k = 5.2 \times 10^{-5}$ M^{-1} s^{-1} $\mu = 1$ M by the isotopic exchange method[7]) which is a dramatic difference considering the Co^{II}sep salt has the normal paramagnetism for high spin Co(II) ($\mu_{eff} = 4.72$ μ_B) and has essentially the same ligand field spectrum as the tris(ethylenediamine) molecule.[8] The Co(III) ions show analogous properties. At present we have no clear understanding of this pronounced electron transfer difference.

The apparent consequences of this work are that numerous metal ions, the complexes of which are normally labile, will become kinetically inert with stable chiral forms. All the chemistry will be mononuclear and therefore interesting in those areas where polymers are frequently observed, e.g., Mo and W. Stabilization of mononuclear Rh(II) and Pt(III) is a possibility and there will be a range of very stable oxidants and reductants for use in inorganic and organic chemistry, both for synthesis and as mechanistic probes, unfettered by the hydrolysis problems which frequently plague the use of aqua ions. Also there is a prospect for the use of the ligands as therapeutic agents. These aspects are currently being investigated with complexes derived from capping tris(ethylenediamine) and 1,1,1-tris(4-amino-2-azabutyl)ethane (sen) complexes with tris(methyleneamino) and substituted tris(methylenemethane) moieties.

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Supplementary Material Available: Five tables, listing final crystal parameters, distances and angles, thermal displacements, and intensity data (19 pages). Ordering information is given on any current masthead page.

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(9) On leave from the Chemistry Department, The Royal Veterinary and Agricultural University, DK-1871 Copenhagen V, Denmark.

I. I. Creaser, J. MacB. Harrowfield, A. J. Herlt
A. M. Sargeson,* J. Springborg[9]
Research School of Chemistry
Australian National University
Canberra 2600, A.C.T., Australia

R. J. Geue, M. R. Snow
Department of Physical and Inorganic Chemistry
University of Adelaide
Adelaide 5000, South Australia, Australia

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Naphthylboryne: a Monovalent Organoboron Carbene Analogue from Photolysis of Tri-1-naphthylboron

Sir:

With complete exclusion of oxygen and water, in carbon tetrachloride, cyclohexane, and cyclohexene solutions, tri-1-naphthylboron (**1**), when irradiated at wavelengths equal to or longer than its charge transfer maximum[1] at 350 nm, slowly undergoes two primary competing photochemical reactions (eq 1 and 2).