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A Cobalt(II) Cryptate of a Heteroditopic Cryptand L as an Efficient Oxygenation Catalyst of Organic Substrates Using Molecular Oxygen and 2-Methylpropanal

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Introduction

Catalyses by first-row transition metal complexes are closely related to important biological processes like enzymatic oxygenation and hence can lead to potential biomimetic oxygenation models.[1] Besides, such systems are potentially useful as the next-generation low-temperature bleaching agents.[2] There are various reports of catalyzed oxo-transfer reactions where the oxygen atom sources are reagents like iodosylbenzene, peroxy acids, amine oxides, hypochlorite anions, etc. And the catalysts used are mostly transition metal complexes of acyclic Schiff base ligands,[3] porphyrins,[4] and macrocyclic ligands.[5] Catalysts that are able to oxidize organic compounds with molecular oxygen are rapidly gaining importance.[6−9] Transition metal cryptates can be potentially good homogeneous catalysts[10] although no experimental evidence is available to date. Complexation of a metal ion by a specific ligand with a preorganized donor atoms topology, as in a cryptand, may confer upon it special reactivity features. Besides, due to the cryptate effect, a metal ion is held securely inside the cavity of a cryptand and cannot be dislodged easily, making the catalyst stable under experimental conditions. This way the catalyst can be re-used, making the turnover number very high. It has been reported[11] earlier that Co(II) complexes are quite versatile in catalyzing the oxidation of olefins by dioxygen in presence of 2-methylpropanal to epoxides with concomitant co-oxidation of the aldehyde to the carboxylic acid. Herein, we report the first example of a Co(II) cryptate which acts as an efficient oxygenation catalyst at room temperature toward a number of olefinic and benzylic substrates, utilizing molecular oxygen at atmospheric pressure and 2-methylpropanal. We have been able to crystallize the cryptate in the presence of KSCN, whose structure is also described.

Experimental Section

Materials and Measurements. All chemicals were obtained from either Aldrich or SD Fine Chemicals and used as received, but 2-methylpropanal was freshly distilled every time before use. Cobalt(II) picrate was prepared by a literature procedure.[12] All solvents were purified prior to use. Elemental analyses and physical studies were carried out as described elsewhere.[13]

Synthesis of L. The ligand **L** (Figure 1) was prepared as described earlier[13] by [1+1] Schiff base condensation of the tripodal triamine tris(2-aminoethyl)amine with the tripodal trialdehyde tris[2-(3-phenyloxy)ethyl]amine followed by reduction with $NaBH_4$.

[Co(L)](picrate)$_2$ (1). To **L** (0.056 g, 0.1 mmol) dissolved in 5 cm^3 of MeOH was added cobalt(II) picrate (0.052 g, 0.1 mmol) dissolved in 5 cm^3 of MeOH. A yellow solid precipitated immediately and was collected by filtration, washed with MeOH, and air-dried. The solid, upon recrystalization from MeCN, afforded a reddish yellow solid in 85% overall yield, which was dried under vacuum at 40 °C. Anal. Calcd for $C_{45}H_{49}N_{11}O_{17}Co$: C, 50.28; H, 4.59; N, 14.33. Found: C, 50.52; H, 4.39; N, 14.10. FAB-MS: *m/z* 846 (**1** − picrate), 618 (**1** − 2 picrates).

[Co(L)(NCS)](picrate) (2). Complex **1** (0.109 g, 0.1 mmol) was dissolved in 10 cm^3 of MeCN and treated with KSCN (0.010 g, 0.1 mmol) dissolved in 2 cm^3 of MeOH with warming at 50 °C. Upon addition of KSCN, the color of the solution changed to dark green. This solution was filtered, and the filtrate was allowed to evaporate slowly at room temperature. Overnight, dark green crystals appeared, which were collected by filtration and air-dried. A further crop was obtained on further evaporation of the solvent at room temperature. Yield: 81%. Anal. Calcd for $C_{45}H_{49}N_{11}O_{17}Co$: C, 53.09; H, 5.23; N, 13.93. Found: C, 52.85; H, 5.41; N, 14.15.

Caution! The picrate salts must be handled with care as they are potential explosives.

General Oxidation Reactions. All the reactions were carried out under an atmosphere of molecular oxygen at ambient pressure and temperature. In a typical experiment, a substrate (10 mmol) and 2-methylpropanal (20 mmol) were added to MeCN (15 cm^3) containing the cobalt(II) cryptate, **1** (5 mol %), and the mixture was allowed to stir for 12−14 h. Progress of the reaction was monitored by TLC. Aqueous workup followed by column chromatography afforded the corresponding products (Table 3) which were characterized by IR and ^{1}H-NMR techniques. The re-usability of the catalyst was checked with *trans*-stilbene as the substrate, which underwent 100% conversion. We added a fresh batch of a substrate and 2-methylpropanal to the reaction vessel once the first batch of the substrate underwent complete conversion. Each batch containing the same amount of the substrate as well as 2-methylpropanal required the same amount of time for complete conversion, indicating that the catalyst was virtually intact. This process could be repeated at least ten times. Co(II) complexes with acyclic ligands have been used by other workers[7] for similar oxidation reactions. However, none of these reports mention about the reusability of the catalyst.

X-ray Structural Studies. Single-crystal X-ray data for complex **2** was collected at room temperature on an Enraf-Nonius CAD4-Mach diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The crystal data are presented in Table 1. Cell parameters were determined by least-squares refinement of the diffractometer setting angles for 25 centered reflections that were in the range $18° \le 2\theta \le 22°$. Three standard reflections were measured at every hour to monitor instrument and crystal stability. The crystal did not diffract beyond 45° in a significant manner. Besides, the peak profiles were broader than usual due to poor crystallinity although the decay as monitored by three standard reflections was less than 1%. Intensity data were corrected for decay and Lp effects; analytical absorption

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Table 1. Crystallographic and Refinement Data for [Co(**L**)(NCS)](picrate), **2**

empirical formula	$C_{40}H_{47}N_9O_{10}SCo$
MW	904.866
temp, °C	25
radiation, graphite monochromated	Mo Kα
λ, Å	0.710 73
cryst system	monoclinic
space group	$C2/c$
a, Å	47.466(3)
b, Å	10.415(2)
c, Å	17.204(9)
β, deg	93.84(2)
V, Å^3	8485.35(5)
Z	8
F(000), electrons	713
D_{calcd}, g/cm^3	1.417
μ, mm^{-1}	0.52
cryst size, mm^3	0.3 × 0.2 × 0.1
transm factor (max, min)	0.8864, 0.7337
no. of unique reflcns	3924
no. of reflcns used ($I > 2\sigma(I)$)	2158
no. of variables	551
R^a	0.072
$R_w{}^b$	0.070
goodness of fit	5.83

^{a} $R = \sum||F_o| - |F_c||/\sum||F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma(F)$.

corrections were also applied. The XTAL 3.2 program package[14] was used in absorption and all subsequent calculations, utilizing a 486-DX personal computer working under MS-DOS version 5 at 66 MHz. The linear absorption coefficients, scattering factors for the atoms, and the anomalous-dispersion corrections were taken from the usual source.[15] The structure was solved by direct methods[16] and successive difference Fourier syntheses. The refinement was done on F by full-matrix least-squares techniques using anisotropic thermal parameters for all non-hydrogen atoms. Some of the hydrogen atoms could be located in the difference maps; the rest were calculated by assuming ideal geometries of the atoms concerned. H atom positions or thermal parameters were not refined.

Results and Discussion

The cryptand **L** readily forms the mononuclear complex [Co(**L**)](picrate)$_2$ when it is treated with 1 equiv of cobalt(II) picrate. The metal ion occupies the end of the cavity that provides an N_4 donor set. The Co(II) cryptate so formed can be isolated without any difficulty, and it readily takes up an anion like SCN^-, forming a pentacoordinated complex due to coordinative unsaturation present at the metal center.

Description of the Structure of [Co(L)(NCS)](picrate) (2). A perspective view of the molecule giving the atom-numbering scheme is shown in Figure 1, while selected bond distances and angles are collected in Table 2. The molecular structure consists of discrete [Co(**L**)(NCS)]$^+$ cations and picrate anions. This structure was found to be isomorphous with the copper(II) cryptate [Cu(**L**)(NCS)](picrate).[13] The Co(II) ion is coordinated to four N atoms of the tren unit at one end of the cavity. The fifth position is occupied by the N atom of the SCN^- group. Therefore, in the absence of KSCN, the fifth coordination site will either be empty or be occupied by a solvent molecule. The cavity above the tren binding site is skewed away from the metal center and the thiocyanate group. The cryptand is in an endo−endo conformation with the two bridgehead N atoms 8.136(12) Å apart. The free ligand also crystallizes in the endo−endo conformation.[13] The coordination geometry around the Co(II) ion is thus trigonal bipyramidal where the bridgehead N(1) and the N of the thiocyanate group occupy axial positions. The Co ion is 0.414(10) Å above the equatorial plane described by N(2), N(4), and N(5). The Co−N and other bond distances and angles are within normal values. However, the standard deviations of bond distances and angles are higher than what is normally found. This is due to the poor crystallinity of **2**.

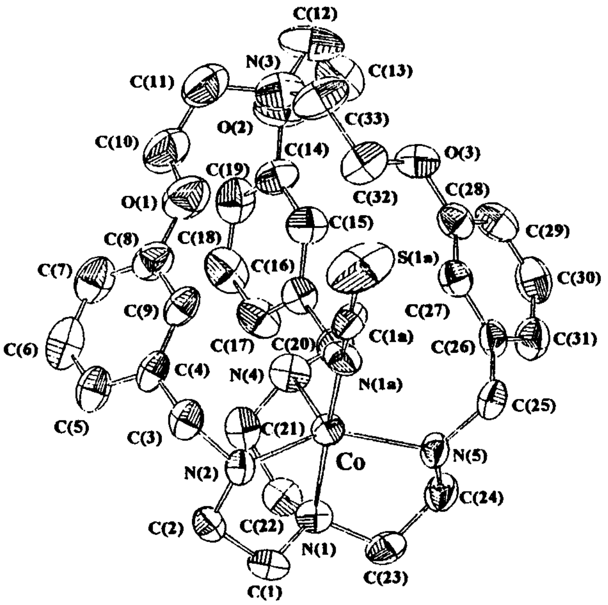

Figure 1. ORTEP[20] drawing of the cation of **2** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Co(**L**)(NCS)](picrate), **2** (Esds in Parentheses)

Co−N(1)	2.194(14)	Co−N(5)	2.102(11)
Co−N(2)	2.174(13)	Co−N(1a)	1.997(10)
Co−N(4)	2.179(16)		
N(1)−Co−N(2)	81(2)	N(1a)−Co−N(1)	168(1)
N(1)−Co−N(4)	80(3)	N(1a)−Co−N(2)	92(4)
N(1)−Co−N(5)	76(2)	N(1a)−Co−N(4)	111(4)
N(2)−Co−N(4)	107(3)	N(1a)−Co−N(5)	100(3)
N(2)−Co−N(5)	129(2)	Co−N(1a)−C(1a)	170(1)
N(4)−Co−N(5)	113(3)		

Spectral and Magnetic Studies. The UV−vis spectra of both **1** and **2** are dominated by strong absorptions from the picrate anion in the near-UV region. High-spin trigonal bipyramidal Co(II) complexes exhibit[17a] a number of bands of moderate intensity starting from the near-UV up to the near-IR. Complex **2** exhibits two well-defined bands at 600 and 720 nm with intensities of 180 and 40 M^{-1} cm^{-1}, respectively, and one weak band at around 1700 nm with an intensity of 35 M^{-1} cm^{-1}. The band positions reported[17b] for the complex [Co(Me$_6$-tren)(NCS)]SCN·H$_2$O from single-crystal polarized spectral studies were at 475, 605, 675, and 1725 nm. Other high-spin trigonal bipyramidal Co(II) complexes exhibit similar band positions.[17a] Complex **1** shows two bands at 715 and 1085 nm with intensities of 120 and 30 M^{-1} cm^{-1}, respectively. The higher energy bands for both **1** and **2** are mixed with intense bands due to the picrate anion. However, the two complexes

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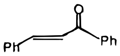
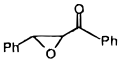
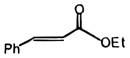
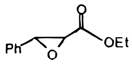
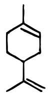
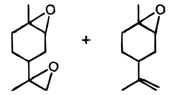
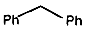
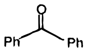
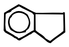
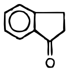
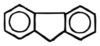
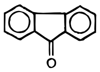
Table 3. Summary of Co(III) Cryptate Catalyzed Oxidation of Olefinic and Benzylic Substrates[a]

Entry	Substrate	Product	Yield %
1			quant.
2			82
3			50
4			quant. (3 : 1)
5			91
6			70
7			49

[a] Products were characterized by IR and ^{1}H NMR spectroscopy. Yields are as isolated for olefinic substrates and ratios determined by ^{1}H NMR, while they are determined by HPLC for benzylic substrates.

exhibit different spectral characteristics. The effective magnetic moment numbers ($\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$) at 300 K for **1** and **2** are 4.11 and 4.80, respectively, which are within the range found for high-spin Co(II) complexes with tetrahedral/trigonal bipyramidal geometry.[17a]

Electrochemistry. Electron transfer properties of the complexes were probed by cyclic voltammetry at 298 K on dinitrogen-flushed solutions in MeCN. None of the complexes show any cyclic responses in the region +1.0 to −1.0 V. This could be due to the rigidity of the N_4 donor set of the cryptand.[13]

Catalytic Behavior of the Cryptate, 1. In **1**, the upper part of the cavity can either be vacant or be occupied by a solvent molecule. Hence, we have probed possible catalytic activity of **1**. Results of our studies are summarized in Table 3. While the olefinic substrates form epoxides, the benzylic substrates are converted to the corresponding ketones in excellent yields. Interestingly, electrophilic olefins also undergo oxidation under such mild conditions, i.e. ambient temperature and pressure. This type of transformation was assumed to occur via high-valent metal−oxo intermediates[18] generated from the catalyst by a number of steps. In a recent paper, Valentine et al.[19] elegantly showed that when metalloporphyrins and metal cyclam complexes were used as catalysts, the role of the metal complexes was to aid in the initiation step for the free radical autoxidation of the aldehyde and that acylperoxy radicals generated in the autoxidation reaction (or metal complexes formed by complexation of the acylperoxy radicals) were the active epoxidizing agents. Likewise, in the case of complex **1**, the acylperoxy radical can complex with the metal ion in the cavity, forming the metal−peroxy complex. This can either transfer the oxygen atom directly to the substrate or form metal−oxo species which can transfer the oxygen to the substrate.

Conclusion. We have shown here that the Co(II) cryptate can act as an efficient oxidizing agent because it occupies only one end of the cavity, keeping the other end vacant. It can be re-used many times without loss of its catalytic activity. Our present aim is to design cryptands containing a chiral unit close to the metal complexing site. This and other related studies are in progress.

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Supporting Information Available: Tables of crystallographic data, non-hydrogen positional, hydrogen positional, and atomic displacement parameters, bond lengths, and bond angles and a packing diagram for **2** (9 pages). One X-ray crystallographic file, in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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