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A Mixed Complex of Sodium and Cobalt(III) with sym-Dibenzo-16-crown-5-oxyacetate, $[(NH_3)_5Co(C_{21}H_{23}O_8)Na](ClO_4)_3 \cdot 2H_2O$

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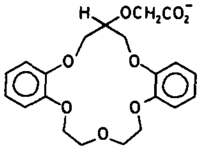
Introduction

Complexation of crown ethers (macrocyclic polyethers) by a wide variety of cations has been reported, including alkali and alkaline earth metal ions [1, 2], ammonium ion [1], hydronium ion [3], the guanidinium ion [4], and transition metal ions [5–12]. It has been found that crown ether oxygen donor atoms exhibit a much weaker affinity for transition metal ions than for metal ions of groups IA and IIA. Thus, crystallographic data for complexes of 18-crown-6 with $Co(H_2O)_6^{2+}$ [9], $Mn(H_2O)_6^{2+}$ [10], and $[Mn(H_2O)_5(NO_3)]^+$ [11] show that the crown ether oxygen atoms prefer hydrogen bonding to the aquo ligands over direct coordination to the metal ion. In contrast, extensive crystallographic documentation exists for direct interactions between crown ether oxygen atoms and representative metal ions [13]. Ligation of transition metal ions by polyether oxygen atoms has been reported only for compounds containing weakly-coordinating counterions or solvent species, *i.e.* $Cu(12\text{-crown}4)Cl_2$ [12] and $Mn(12\text{-crown-}4)_2(Br_3)_2$ [14].

Considerable progress has been made recently in the functionalization and modification of crown ethers [15]. Substituents, such as alkyl and functional groups, may be attached to aliphatic carbon atoms of the macrocyclic ring or to aromatic subunits that are fused to the macrocycle. Introduction of alcohol, amine, thiol, or carboxylic acid functional groups into crown ethers should dramatically increase their affinity for transition metal ions, and permit the synthesis of mixed complexes containing a transition metal ion and a representative metal ion simultaneously coordinated to a common crown ether ligand. We report here the synthesis of a mixed complex of sodium and cobalt(III) with *sym*-dibenzo-16-crown-5-oxyacetate (*I*), $[(NH_3)_5Co(I)Na](ClO_4)_3 \cdot 2H_2O$.



I

Experimental

Materials

Reagent grade chemicals were used throughout. Acetone was doubly-distilled before use. Benzyltrimethylammonium hydroxide, 40% aqueous solution (Hexcel Specialty Chemicals), and SP-Sephadex-C-25 cation exchange resin (Sigma) were used as received. The complexes $[(NH_3)_5Co(H_2O)](ClO_4)_3$ [16] and $[(NH_3)_5Co(DMSO)](ClO_4)_3 \cdot 2H_2O$ [17] were prepared by literature methods. *sym*-Dibenzo-16-crown-5-oxyacetic acid was obtained by the method of Bartsch *et al.* [18].

Spectral Characterization of sym-Dibenzo-16-crown-5-oxyacetic Acid (I-H)

^1H NMR (dimethyl sulfoxide-d^6): δ 6.90 (s, 8, aromatic protons); 4.34, 4.13, 4.00, 3.83, 3.75 (m, 15, overlapping resonances of methylene protons). IR (KBr pellet): 3390 (m, broad), 3000 (sh), 2900 (m), 2850 (m), 1720 (s), 1580 (m), 1488 (vs), 1440 (s), 1348 (w), 1317 (w), 1242 (vs), 1200 (vs), 1110 (vs), 1073 (m), 1054 (m), 1035 (sh), 1008 (m), 973 (w), 922 (m), 842 (w), 828 (sh), 728 (s) cm^{-1}. UV (CH_3CN): λ_{max} (log ϵ) 275 (sh, 3.65), 272 (3.66) nm.

Preparation of $[(NH_3)_5Co(I)Na](ClO_4)_3 \cdot 2H_2O$

The target complex was prepared from both $[(NH_3)_5Co(H_2O)](ClO_4)_3$ and $[(NH_3)_5Co(DMSO)](ClO_4)_3 \cdot 2H_2O$. In the preferred synthetic route, 3.88 g of *I*-H (9.60 mmol) was mixed with 50 ml of acetone. Sufficient sodium hydride (0.176 g, 7.2 mmol) was then added, with stirring to neutralize 75% of the carboxylic acid. At this point, some of the ligand remained undissolved. $[(NH_3)_5Co(DMSO)]$ $(ClO_4)_3 \cdot 2H_2O$ (0.502 g, 0.90 mmol) dissolved in a small amount of acetone was added slowly, and the resulting mixture was refluxed for 8.5 h. After cooling to room temperature, undissolved *I*-H was separated from the red solution by filtration. The solvent was partially removed *in vacuo*, which produced a slurry. Chloroform (70 ml) was added, and the resulting clear, orange solution was saturated with $NaClO_4 \cdot H_2O$. A pink compound was isolated by filtration after overnight storage of the solution at –15 °C. The solid was washed with triply-distilled water to remove excess $NaClO_4$,

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and was dried *in vacuo* at room temperature; yield: 1.2 g.

The crude product was invariably found to be contaminated with *I*-H, and impurity that could not be removed by recrystallization of the complex from water. Purification was therefore achieved through cation exchange chromatography. The pink compound (2.0 g) was dissolved in 50% (V/V) acetone–water and loaded into a 14 X 3 cm SP C-25 column (Na^+ form) which had been equilibrated with the same solvent mixture. *I*-H was then washed through the column by elution with 400 ml of 50% acetone–water, leaving a single, broad pink band at the top of the column. The complex was eluted with 0.2 *M* $NaClO_4$ in 50% acetone–water over a period of 10 hours, yielding 480 ml of solution. No other bands were observed.

Acetone was removed from the eluate *in vacuo* until precipitation commenced, followed by cooling in an ice-salt bath. The pink precipitate was washed with ice-cold water and ether, and then dried *in vacuo* at room temperature; yield: 0.47 g. *Anal.* Calcd for $[(NH_3)_5Co(I)Na](ClO_4)_3\cdot 2H_2O$: C, 27.86%; H, 4.64%; N, 7.74%; Cl, 11.78%, Co, 6.51%; Na, 2.54%. Found: C, 28.00%; H, 4.55%, N, 7.69%; Cl, 11.11%; Co, 6.40%; Na, 1.90%. ^1H NMR (acetone-d^6): δ 7.02 (s, 8, aromatic protons); 4.49, 4.31, 4.15, 3.96 (m, 29 ± 1, overlapping resonances of methylene and ammine protons). IR (KBr pellet): 3390 (s, broad), 3200 (vs, broad), 2890 (w), 2850 (w), 1605 (s, broad), 1575 (sh), 1485 (s), 1437 (m), 1380 (m), 1290 (s), 1234 (vs), 1198 (s), 1090 (sh), 1070 (vs, broad), 1038 (sh), 1003 (w), 915 (w), 830 (m), 810 (sh), 770 (w), 732 (m) cm^{-1}. UV/VIS (H_2O): λ_{max} (log ϵ) 501 (1.87), 344 (1.90), 269 (3.78) nm.

A purple by-product was observed in the preparation of $[(NH_3)_5Co(I)Na](ClO_4)_3\cdot 2H_2O$ from aquopentaamminecobalt(III) perchlorate in aqueous solution. The pH of a suspension of *I*-H (4.39 g, 10.9 mmol) in 30 ml of water was adjusted to 12.8 by the addition of 40% benzyltrimethylammonium hydroxide. The suspension was stirred overnight at room temperature, filtered, and then adjusted to pH 5.5 by slowly adding 70% $HClO_4$. This acidification of the solution caused the precipitation of some of the crown ether components. The suspension was heated at 60 °C while 0.50 g (1.1 mmol) of $[(NH_3)_5Co(H_2O)](ClO_4)_3$, dissolved in 5 ml of water, was slowly added. The reaction was allowed to proceed for 10 h, after which a purple solid mixed with undissolved *I*-H was observed. The precipitate was collected and washed with acetone, yielding a purple solution which passed through the filter and a residue of *I*-H. Most of the solvent was removed from the purple solution *in vacuo*, after which a solid was obtained by adding diethyl ether. The solid was collected and dried *in vacuo* at room temperature; yield: 0.6 g.

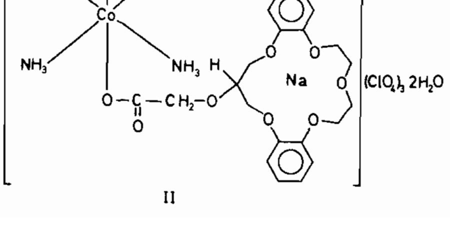
This crude purple solid (0.5 g) was resolved into two components through chromatography on SP-C-25 resin, using 50% water–acetone as the solvent. After loading, the 16 X 2.5 cm column was eluted with 0.2 *M* $NaClO_4$ in 50% water–acetone. A purple band, well-separated from the trailing pink component, was eluted in 35 ml over a period of 1.25 h. Elution of the pink band (350 ml eluate) required 8.5 h. Solid complexes were derived from the eluate solutions by partial evaporation of the solvent and cooling in an ice–salt bath. The products were dried *in vacuo* after washing with small portions of ice-cold water and ether; yields: 0.10 g of purple complex and 0.12 g of pink complex. Characterization of the purple complex: *Anal.* Calcd. for *cis*-$[(NH_3)_4Co(I)_2Na_2](ClO_4)_3\cdot I\text{-}H\cdot C_3H_6O$: C, 45.53%; H, 5.06%; N, 3.22%; Cl, 6.12%; Co, 3.39%; Na, 2.64%. Found: C, 45.64%; H, 5.20%; N, 2.92%; Cl, 6.05%; Co, 2.90%; Na, 2.99%. ^1H NMR (acetone-d^6). δ 7. 01 (s, 24, aromatic protons); 4.45, 4.32, 4.13 (m, 55 ± 2, overlapping resonances of methylene and ammine protons). IR (KBr pellet): 3400 (sh), 3290 (m, broad), 2900 (m), 2850 (m), 1720 (sh), 1685 (m), 1605 (sh), 1578 (s), 1484 (vs), 1438 (s), 1380 (m, broad), 1290 (s), 1235 (vs), 1198 (vs), 1105 (sh), 1074 (vs, braod), 1036 (sh), 1005 (sh), 915 (m), 828 (sh), 810 (m), 770 (m), 732 (s) cm^{-1}. UV/VIS (CH_3CN): λ_{max} (log ϵ) 532 (2.00), 372 (sh, 2.05), 276 (sh), 272 (4.40) nm.

Instrumentation

UV–visible spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were obtained from a Beckman Acculab 8 instrument. A Varian EM-360 spectrometer was employed for nuclear magnetic resonance measurements, using tetramethylsilane as internal standard.

Results and Discussion

Elemental analysis, NMR, IR and UV–visible results strongly support the formulation of the pink complex as $[(NH_3)_5Co(I)Na](ClO_4)_3\cdot 2H_2O$, with structure as shown in *II.*



II

Spectral comparisons for the complexes derived from $[(NH_3)_5Co(H_2O)]^{3+}$ and $[(NH_3)_5Co(DMSO)]^{3+}$ show that the products are identical. The positions and intensities of the ligand field transitions at 501 and 344 nm agree well with values reported for many other carboxylatopentaamminecobalt(III) ions [19]. The presence of a coordinated carboxylate group is further indicated by the $-COO^-$ antisymmetric and symmetric stretching vibrations, observed at 1605 and 1380 cm^{-1}, respectively. Although the proton NMR spectrum is not sufficiently resolved to provide useful structural information, comparisons of integrated intensities between the singlet at 7.02 ppm and the sum of resonances appearing in the interval 3.96–4.49 ppm is 8:29 ± 1, consistent with the assignment of the singlet to 8 aromatic protons and the remaining resonances to 15 ammine and 15 methylene protons. While the broad IR absorption at 3390 cm^{-1} clearly demonstrates the presence of water, there is some uncertainty concerning the number of H_2O molecules of crystallization present. Reasonable, but not excellent, agreement between theoretical and actual elemental analyses is also found for formulas including one or three H_2O molecules.

By analogy to well-known crown-ether chemistry, the most likely binding site for the sodium ion is within the cavity of the macrocyclic ring, where it may interact with several polyether oxygen atoms. The diameters of Na^+ and the ring cavity of acid-16-crown-5 are estimated [20] to be 1.96 and 2.0–2.4 Å, respectively, which suggests the feasibility of strong complexation. Infrared absorptions of $[(NH_3)_5Co(\mathit{l})Na](ClO_4)_3 \cdot 2H_2O$ in the range of 1100–1600 cm^{-1} are shifted to slightly lower frequencies, by 2–10 cm^{-1}, relative to those of the free crown ether. Similar small perturbations in the infrared spectra of alkali metal–crown ether complexes have been attributed to coordination of the metal ion by macrocyclic ring oxygen atoms [21, 22].

The pink complex is soluble in water, acetone, dimethyl sulfoxide, and acetonitrile; but insoluble in methanol, chloroform, and ether. The solubility characteristics of the pink and purple complexes are identical, except that the latter has insufficient solubility in water to allow precise spectroscopic measurements to be made in this solvent. The $[(NH_3)_5Co(\mathit{l})Na]^{3+}$ ion is quite stable towards loss of the crown ether ligand. The visible absorption spectrum of the complex remained essentially unchanged after heating a pH 4 solution at 70 °C for 8 h.

We cannot presently make a definitive assignment of the formula and structure of the unexpected purple product. Elemental analysis, uv–visible [23], infrared [24], and nmr data are consistent with the fomula *cis*-$[(NH_3)_4Co(\mathit{l})_2Na_2](ClO_4)_3 \cdot \mathit{l}\text{-}H \cdot C_3H_6O$, containing an acetone molecule of crystallization and a molecule of unionized crown ether not directly coordinated to cobalt(III).

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