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ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · MAY 1989

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Synthesis of Cobalt(III) "Cage" Complexes

A Twist on an Old Theme in the Inorganic Laboratory

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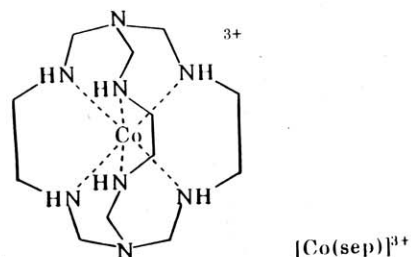
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It is likely that at any given moment of time, some undergraduate, somewhere in the world, is preparing a sample of tris(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_3]\text{Cl}_3$. The synthesis is straightforward (1) and even the occasional failure results in interestingly colored solutions. The method of preparation and the complex itself can be used to demonstrate a range of important inorganic chemical concepts.

$[\text{Co}(\text{en})_3]\text{Cl}_3$ has been used as the starting material for the synthesis of a range of encapsulated cobalt(III) compounds in which the cobalt(III) ion is "trapped" in a macrobicyclic cage (2-4). The properties and reactions of these cage compounds are, if anything, more interesting than those of the parent compound. A synthesis of one of these compounds, $[\text{Co}(\text{dinosar})]\text{Br}_3$ (dinosar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) has appeared in *this Journal* (5). The synthesis described for this compound is particularly attractive as an undergraduate experiment because the complex crystallizes from solution during the preparation removing the necessity of extensive and time-consuming chromatographic purification, which typifies most of these syntheses.

Recently, we have reported the reaction of the cage complex $[(1\text{-amino-8-methyl-3,6,9,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III)}]\text{chloride}$, $[\text{Co}(\text{AMMEsarH})]^{4+}$, with dithiocarbamate anions, $[\text{S}_2\text{CNR}_2]^-$ to give the salts $[\text{Co}(\text{AMMEsar})][\text{S}_2\text{CNR}_2]_3$ (6). Unlike the typical salts of the cage compounds (Cl^- , Br^- , ClO_4^-), which are soluble in aqueous solution, the dithiocarbamate salts of the cages are insoluble in aqueous solution, but extremely soluble in organic solvents such as chloroform, methylene chloride, and toluene. By contrast with the integrity of the dithiocarbamate anion being maintained in these compounds, addition of a sodium dithiocarbamate to $[\text{Co}(\text{en})_3]\text{Cl}_3$ results initially

in the formation of the $[\text{Co}(\text{en})_3][\text{dtc}]_3$ salt, which, slowly in the solid state and rapidly in solution, transforms to the green $\text{Co}(\text{dtc})_3$ complex with the ejection of the ethylenediamine ligands. While this ligand substitution reaction is interesting in its own right, the different behavior of the encapsulated (i.e., $[\text{Co}(\text{AMMEsarH})]^{4+}$) and unenclosed ($[\text{Co}(\text{en})_3]^{3+}$) complexes in the presence of the dithiocarbamate ligand suggested a method of isolating cage complexes without use of extensive chromatographic separations. The complex chosen for this experiment is $[\text{Co}(\text{sep})]^{3+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane), an analogue of $[\text{Co}(\text{dinosar})]^{3+}$, e.g.,



The preparation of this complex was first reported in 1977 (2) and has been reported subsequently (3,7). Reaction between $[\text{Co}(\text{en})_3]\text{Cl}_3$, formaldehyde, and ammonia, under conditions where the reactants were slowly added to a stirred aqueous solution of metal complex in the presence of base, and subsequent workup employing cation exchange chromatography, results in high yield of the desired product. This preparative procedure has previously been dismissed as unsuitable for the undergraduate laboratory because of the necessary chromatographic isolation procedure (5). We now

wish to report a procedure we use in our classes that allows the $[\text{Co}(\text{sep})]^{3+}$ ion to be precipitated from the capping mixture as the $[\text{S}_2\text{CNET}_2]^-$ salt. Subsequently, $[\text{Co}(\text{sep})]\text{Cl}_3$ is simply prepared by decomposing the dithiocarbamate anion with hydrochloric acid if the chloride salt is desired, although any acid, HX , may be employed ($\text{X} = \text{Br}^-, \text{SO}_4^{2-}, \text{CF}_3\text{SO}_3^-$). This synthetic approach removes the necessity for chromatographic procedures and permits ready synthesis of two cage complexes, $[\text{Co}(\text{sep})]\text{Cl}_3$ and $[\text{Co}(\text{dinosar})]\text{Br}_3$, in the undergraduate laboratory. Moreover, reaction between $[\text{Co}(\text{sep})]\text{Cl}_3$ and any sodium N,N' -dialkylthiocarbamate salt in aqueous solution results in precipitation of further cage-dithiocarbamate salts, offering the possibility of comparative studies of the spectroscopic properties of the anions.

The different approaches employed in the syntheses illustrate a number of important and useful chemical exercises. The synthesis described can be completed in a 4-h laboratory session, or over two days in tandem with or consequential to the synthesis of $[\text{Co}(\text{en})_3]\text{Cl}_3$. The use of the dithiocarbamate anion as a "soap" demonstrates clearly the phase transfer properties of this ligand. The differences in the reaction of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{en})_3]\text{Cl}_3$ and $[\text{Co}(\text{sep})]\text{Cl}_3$ upon addition of the dithiocarbamate salt demonstrate nicely the effects of chelation and the macrobicyclic environment engendered by the three-dimensional cage ligand.

The visible spectra of the $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ and $[\text{Co}(\text{sep})]\text{Cl}_3$ can be compared and the origins of the intense coloration of the dithiocarbamate salt discussed. In addition, the infrared and nuclear magnetic resonance spectra of the complexes can be investigated.

Synthesis of the Macrobicyclic Complex

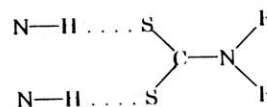
Separate solutions of 37% aqueous formaldehyde (50 mL) (caution: the reaction should be performed in a fume hood) and concentrated aqueous ammonia (14 mL diluted to 50 mL) were slowly added over a period of 1 h to a stirred aqueous suspension (20 mL) of Li_2CO_3 (2.3 g) and $\pm[\text{Co}(\text{en})_3]\text{Cl}_3$ (0.9 g). We employ a peristaltic pump for the additions; however, any device that will control the addition rate at approximately 1 mL/min will suffice, e.g., 50-mL syringes fitted with the appropriate gauge needle and using gravity feed are effective. After completion of the addition, the mixture was stirred for a further 15–20 min, and then the unreacted Li_2CO_3 was removed by filtration. A solution of $\text{Na}[\text{S}_2\text{CNET}_2] \cdot 3\text{H}_2\text{O}$ (8) (2.5 g) in 50 mL of water was added to the filtrate and the mixture stirred for a further 30 min. The resultant mixed precipitate of red $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ and some green $\text{Co}(\text{S}_2\text{CNET}_2)_3$ was washed with 3×50 mL portions of a 20:80 mixture of methylene chloride and hexane to remove the $\text{Co}(\text{dtc})_3$ complex. This complex is presumably formed by complexation of the dithiocarbamate anion with cobalt cations extracted from the various uncaged cobalt(III) species formed as byproducts of the reaction or from the unreacted starting material. The yield of the cage dithiocarbamate salt was 1.25 g (60%).

The $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ (0.5 g) complex was suspended in acetonitrile (10 mL) and a few drops of concentrated hydrochloric acid added. The dithiocarbamate anion decomposed rapidly and the resulting pale yellow solution was warmed on a hot plate for 10 min then permitted to cool slowly resulting in crystals of $[\text{Co}(\text{sep})]\text{Cl}_3$. (Yield 0.27 g, 94%.)

Characterization of the Complexes

Electronic Spectra. The $[\text{Co}(\text{sep})]\text{Cl}_3$ complex has absorption maxima in the visible region at 475 nm (ϵ 107 $\text{M}^{-1}\text{cm}^{-1}$) and 340 nm (ϵ 116) (2, 7). The $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ complex exhibits a broad charge-transfer band that all but obscures the d-d transitions due to the CoN_6 chromophore. Inflections at ~ 470 and 340 nm are still observable.

Infrared Spectra. The infrared spectra of $[\text{Co}(\text{sep})]\text{Cl}_3$ shows a strong N-H stretching vibration at 3040 cm^{-1} . In the dithiocarbamate salt it appears that the formation of strong hydrogen bonds between the secondary amine protons and the sulfur atoms (6) shifts this band to 2850 cm^{-1} :



A similar mode of bonding has been observed in the cobalt(II) complex $[\text{Co}(\text{sep})][\text{S}_2\text{O}_6] \cdot \text{H}_2\text{O}$ where the dithionate ion forms pairs of contacts with the protons of the coordinated secondary nitrogens (3).

NMR Spectra. The ^{13}C NMR spectrum of $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ (Bruker WM250 spectrometer, CDCl_3 , shifts relative to Me_4Si , positive downfield) exhibits four resonances of equal intensity at +11.8 (CH_3 , dtc), +47.9 (CH_2 , dtc), +54.0 (CH_2 of the ethylenediamine ring residues), +68.1 (CH_2 in each cap), and a weak resonance at +206 ppm (CS_2). For $[\text{Co}(\text{sep})]\text{Cl}_3$ the ^{13}C NMR spectrum (D_2O , shifts relative to dioxan, positive downfield) two resonances of equal intensity are observed at -13.2 (CH_2 of the ethylenediamine ring residues) and +0.4 ppm (CH_2 in each cap) (2, 7). The ^1H NMR spectra are more complicated. For $[\text{Co}(\text{sep})]\text{Cl}_3$ (D_2O , shifts relative to TPS) the methylene protons in the cap exhibit an AB doublet pair at 4 ppm ($J \approx 12\text{ Hz}$) while the protons from the ethylenediamine methylene groups exhibit an AA'BB' pattern at 3.2 ppm (2, 7). For $[\text{Co}(\text{sep})][\text{S}_2\text{CNET}_2]_3$ (Varian EM360 60-MHz spectrometer, CDCl_3 , shifts relative to Me_4Si) the spectrum is more complex with a quartet at 4 ppm (CH_2 , dtc), overlapping resonances attributable to protons from the cage at 3.5 ppm, and a triplet at 1.2 ppm (CH_3 , dtc). A broad resonance assigned to the hydrogen-bonded protons of the secondary amines on the cage is observed at 8.8 ppm.

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