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THE GEOMETRICAL ISOMERISM OF $[CoBr(Hedta)]^-$

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The $[CoBr(Hedta)]^-$ complex prepared by the method of Schwarzenbach has been believed to consist of two geometric isomers. However, it was found that one of these two isomers was not the bromo complex, but the chloro complex.

All complexes of the type, $[CoX(Hedta)]^{n-}$($X = NO_2^-$, H_2O, and Cl^-), are known to yield a single geometric isomer, where Hedta denotes a quinquedentate ethylenediaminetetraacetate ligand with a free acetate branch. On the other hand, the $[CoBr(Hedta)]^-$ complex prepared by the method of Schwarzenbach1) has been reported to consist of two geometric isomers by studies of the ring-closure reaction2-4) ($[CoBr(Hedta)]^- \longrightarrow [Co(edta)]^-$) and ^{13}C-NMR spectra,5) although Schwarzenbach described his complex as a single species. However, no attempt has been made to separate these isomers. This letter deals with the separation and characterization of the isomers of the bromo complex produced by the method of Schwarzenbach.

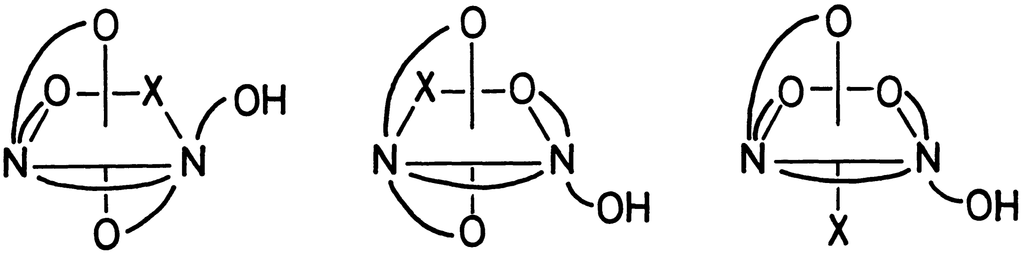
According to the method of Schwarzenbach, the bromo complex was prepared from $CoCl_2 \cdot 6H_2O$, $edta^{4-}$, and an oxidizing agent Br_2. The product was dissolved in cold water, and the solution was poured into a DEAE-Sephadex column in the chloride form (ϕ 3 x 50 cm). The adsorbed blue-green band was eluted with a 0.15M $CaCl_2$ solution to give three separate bands. The first violet band was $[Co(edta)]^-$. The fractions of the second dark blue and the third peacock green bands were collected separately and poured again on DEAE-Sephadex columns after dilution with water. The adsorbed complexes were eluted with a 2M NaCl solution, and the effluents were mixed with a few drops of concd HCl. On cooling in an ice bath, the effluents of the second and the third bands gave dark blue(A) and blue green(B) crystals, respectively.

The blue green complex(B) shows absorption and ^{13}C-NMR spectra identical with those of the bromo complex prepared by the reaction of $[Co(edta)]^-$ with concd HBr. This reaction is known to yield a single isomer of the bromo complex.4,5) The complex(B) gives satisfactory analytical values for the bromo complex. Found: C, 24.44; H, 3.33; N, 5.84; Br, 16.99%. Calcd for $Na[CoBr(Hedta)] \cdot 2H_2O$: C, 24.66; H, 3.52; N, 5.75; Br, 16.41%. On the other hand, the dark blue complex(A) exhibits the same absorption and ^{13}C-NMR spectra as those of the chloro complex.5) The complex(A) is found to contain no bromide ions by qualitative analysis,6) and identified as the chloro complex by elemental analysis. Found: C, 27.62; H, 3.74; N, 6.87; Cl, 8.31%. Calcd for $Na[CoCl(Hedta)] \cdot 1.5H_2O$: C, 27.70; H, 3.72; N, 6.46; Cl, 8.17%.

The formation of the chloro complex should result from the use of $CoCl_2 \cdot 6H_2O$

as the starting material. To confirm this, the bromo complex was prepared by use of $CoBr_2 \cdot 6H_2O$ in place of $CoCl_2 \cdot 6H_2O$. The product contains only one species which is identical with the complex(B). These results lead to the conclusion that one of the so called two isomeric bromo complexes obtained by the method of Schwarzenbach is not the bromo complex, but the chloro complex.

A complex of the type, $[CoX(Hedta)]^{n-}$, has three possible geometric isomers as shown in the Figure. All complexes of this type (X = NO_2^-, H_2O, and Cl^-) have been assigned to *cis*-equatorial structure(I) on the basis of absorption,[7,8] ^1H-,[9] and ^{13}C-NMR spectra.[5] The present bromo complex(B) shows no splitting in the first absorption band, indicating a *mer*(O)*cis*(N)-$[CoBrN_2O_3]$ type,[9] and hence can be assigned to either structure(I) or structure(II). Since no complex of structure(II) is known for edta complexes, the complex(B) may also have structure(I). This assignment will be supported by ^{13}C-NMR studies. A $[CoX(Hedta)]^{n-}$ complex generally exhibits a complicated spectrum (15.04 MHz). However, the resonance peak of a free carboxylate in such a complex can be assigned easily, since its chemical shift shows large pH dependence. The resonance intensity of the free carboxylate in highly soluble, deprotonated $[CoBr(edta)]^{2-}$ (173.5 ppm from TMS in D_2O) is nearly the same as that of $[CoBr(D_4\text{-edta})]^{2-}$ derived from $[Co(D_4\text{-edta})]^-$ in which the four methylene protons of two axial acetate groups are selectively deuterated.[5] Resonance peaks due to carboxylate carbons in $[CoX(Hedta)]^{n-}$ are reported to reduce their intensities on deuteration of the methylene protons of acetate groups.[5] Thus, the complex(B) has a free, undeuterated equatorial acetate branch, and is assigned to structure(I).



(I) *cis*-equatorial (II) *trans*-equatorial (III) polar

Figure Possible geometric isomers of $[CoX(Hedta)]^{n-}$

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