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SYNTHESES, CHARACTERIZATIONS, AND KINETIC ASPECTS OF THIOCYANATO AND ISOTHIOCYANATO LINKAGE ISOMERS OF COBALT(III) COMPLEXES LIGATING AMINOPOLYCARBOXYLATES

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Two pairs of linkage isomers ($[Co(SCN)(edta)]^{2-}$ and $[Co(NCS)(edta)]^{2-}$; $[Co(SCN)(hedtra)]^-$ and $[Co(NCS)(hedtra)]^-$) were prepared. Where $edta^{4-}$ and $hedtra^{3-}$ denote ethylenediaminetetraacetate and N-hydroxyethylethylenediaminetriacetate, respectively. In aqueous solutions at room temperature, the N-bonded isomers were stable, while the S-bonded isomers were unstable : $[Co(SCN)(edta)]^{2-}$ gave $[Co(edta)]^-$. $[Co(SCN)(hedtra)]^-$ gave both $[Co(H_2O)(hedtra)]$ and $[Co(NCS)(hedtra)]^-$.

Much attention has been paid for the thiocyanato (S-bonded) and isothiocyanato (N-bonded) linkage isomerism.[1)] The coordination mode of the thiocyanate to a metal ion has been believed to provide a good criterion for classifying whether the metal ion is hard or soft.[2)] Several linkage isomer pairs of cobalt(III) complexes have been reported so far.[3-7)] Both of linkage isomers were isolated for $[Co(CNS)(NH_3)_5]^{2+}$[8)] and $[Co(CNS)(CN)_5]^{3-}$ respectively. N-Bonded isomer is more stable than S-bonded isomer in the former case and the reverse is true in the latter case. Quite different synthetic routes were employed to synthesize the respective thiocyanato and isothiocyanato isomers.[3-6)]

Our attempt to prepare new complexes $[Co(CNS)L]^{n-}$ led unexpectedly to the simultaneous formation of both S-bonded and N-bonded thiocyanato complexes. Where L denotes ethylenediamine-N,N,N',N'-tetraacetate ($edta^{4-}$) or N-hydroxyethyl-ethylenediamine-N,N',N'-triacetate ($hedtra^{3-}$). This paper describes the syntheses of two linkage isomer pairs and some kinetic aspects on the interconversion of these and related complexes. The present results may serve for better understanding of thiocyanato and isothiocyanato linkage isomerism.

A pair of linkage isomers $[Co(CNS)(hedtra)]^-$ was prepared by heating an aqueous solution (10 ml) containing 2.9 g of NaSCN and 2 g of $[Co(H_2O)(hedtra)]\cdot 2H_2O$ at 60 °C for 5 min. The solution was diluted and passed through QAE Sephadex A-25 anion exchange column(2.6 cm x 30 cm). The adsorbed species were eluted with aqueous KCl solutions. Blue and violet species were eluted in this order. The concentration of the eluate containing the blue species (NH_4Br medium) gave blue crystals of $NH_4[Co(SCN)(hedtra)]\cdot 0.3H_2O$ upon the addition of methanol. Yield : 26.8% vs. $[Co(H_2O)(hedtra)]$. Found : C, 31.98; H, 4.70; N, 13.48%. Calcd for

$NH_4[Co(SCN)(hedtra)]\cdot0.3H_2O$: C, 31.78; H, 4.75; N, 13.48%.

The concentration of the solution containing the violet species gave violet crystals of $K[Co(NCS)(hedtra)]\cdot2.5H_2O$ upon the addition of small amount of ethanol. Yield : 29.0%. Found : C, 27.66; H, 4.51; N, 8.64%. Calcd for $K[Co(NCS)(hedtra)]\cdot2.5H_2O$: C, 27.73; H, 4.23; N, 8.82%.

A pair of linkage isomers $[Co(CNS)(edta)]^{2-}$ was prepared from NaSCN and $Na[Co(edta)]\cdot4H_2O$. An aqueous 1 M $HClO_4$ solution (10 ml) containing $Na[Co(edta)]\cdot4H_2O$ (2.2 g) was heated at 60 °C for 10 min.[9,10] Then, 2.4 g of NaSCN was added and the solution was heated at 90 °C for 1 min. After filtration, the filtrate was diluted and treated as $[Co(CNS)(hedtra)]^-$. The chromatographic separation gave the solutions of $[Co(H_2O)(Hedta)]$, $[Co(edta)]^-$, $[Co(SCN)(edta)]^{2-}$, and $[Co(NCS)(edta)]^{2-}$. The concentration of the latter two solutions yielded blue species $K[Co(SCN)(Hedta)]\cdot KCl\cdot5H_2O$ and violet species $K[Co(NCS)(Hedta)]\cdot2.5H_2O$, respectively, upon the addition of 2 ml of 2 M HCl and small amount of ethanol. Yield of $K[Co(SCN)(Hedta)]\cdot KCl\cdot5H_2O$: 14.0% vs. $Na[Co(edta)]$. Found : C, 21.64; H, 3.23; N, 6.24%. Calcd for $K[Co(SCN)(Hedta)]\cdot KCl\cdot5H_2O$: C, 21.66; H, 3.80; N, 6.88%. Yield of $K[Co(NCS)(Hedta)]\cdot2.5H_2O$: 17.9%. Found : C, 26.73; H, 3.27; N, 8.70%. Calcd for $K[Co(NCS)(Hedta)]\cdot2.5H_2O$: C, 26.94; H, 3.70; N, 8.57%. The analytical result of the former is not satisfactory. This probably comes from the instability and the hygroscopic nature of the compound. However, the molar ratio of cobalt to SCN^- was found to be unity.

The coordination modes of thiocyanate in these four complexes were determined by electronic, infrared absorption, and ^{13}C-NMR spectroscopy. Numerical data of these complexes are listed in Table 1. The first d-d absorption maxima of all four compounds appear at reasonable positions with respect to the spectrochemical series.[11-15] An additional evidence for S-bonded mode in $[Co(SCN)(hedtra)]^-$ and $[Co(SCN)(Hedta)]^-$ is an intense band near 310 nm, which is characteristic of the S-bonded compounds.[16]

The four compounds show very similar infrared spectra one another, except C-N stretching region near 2,100 cm^{-1} due to thiocyanate. Frequency of $\nu(CN)$ of $NH_4[Co(SCN)(hedtra)]\cdot0.3H_2O$ is higher than that of $K[Co(NCS)(hedtra)]\cdot2.5H_2O$ and the intensity of $\nu(CN)$ of the former is lower than that of the latter. A similar relation to this is also seen between $K[Co(SCN)(Hedta)]\cdot KCl\cdot5H_2O$ and $K[Co(NCS)(Hedta)]\cdot2.5H_2O$. These phenomena are consistent with the observation reported for other thiocyanato and isothiocyanato linkage isomers.[17, 18]

^{13}C-NMR spectra of the complexes in D_2O also support the assignment of the coordination mode of thiocyanate ions. The chemical shifts of the coordinated $^{13}CNS^-$ relative to Me_4Si are 125.5 ppm for $NH_4[Co(SCN)(hedtra)]$ and 141.1 ppm for $K[Co(NCS)(hedtra)]$, respectively. These values are consistent with the previously reported ^{13}C-NMR data[19] for the compounds containing N- and S-bonded thiocyanates.

N-Bonded complexes $[Co(NCS)(hedtra)]^-$ and $[Co(NCS)(edta)]^{2-}$ were stable in aqueous solutions at room temperature for a week. No spectral changes were found for both complexes even after heating at 50 °C for 2 h. To the contrary, S-bonded complexes $[Co(SCN)(hedtra)]^-$ and $[Co(SCN)(edta)]^{2-}$ in aqueous solutions were unstable. Simultaneous occurrence of both aquation and linkage isomerization was

Table 1. Spectral data of thiocyanato- and isothiocyanato-(aminopolycarboxylato)cobaltate(III) complexes

Complex	Electronic absorption λ_{max} / nm$^{a)}$		IR absorption ν(CN) / cm^{-1}	^{13}CNS$^-$ Chem. Shift / δppm$^{b)}$
$K[Co(NCS)(hedtra)]\cdot 2.5H_2O$	547 (2.60)	310$^{c)}$ (3.43)	2090	141.1
	225 (4.27)			
$K[Co(NCS)(Hedta)]\cdot 2.5H_2O$	547 (2.60)	221 (4.27)	2120	140.9
$NH_4[Co(SCN)(hedtra)]\cdot 0.3H_2O$	586 (2.39)	387$^{c)}$ (2.53)	2100	125.5
	312 (4.20)	231 (4.18)		
$K[Co(SCN)(Hedta)]\cdot KCl\cdot 5H_2O$	586 (2.37)	402$^{c)}$ (2.42)	2130	——
	312 (4.20)	221 (4.26)		

a) The values in parentheses are log{ε/(M^{-1} cm^{-1})}.
b) Relative to tetramethylsilane (Me_4Si). c) Shoulder.

observed for $[Co(SCN)(hedtra)]^-$.

$$[\mathrm{Co(SCN)(hedtra)}]^- \begin{cases} \xrightarrow{\text{linkage isomerization}\quad k_{is}} [\mathrm{Co(NCS)(hedtra)}]^- & (1) \\ \xrightarrow{\text{aquation}\quad k_{aq}} [\mathrm{Co(H_2O)(hedtra)}] + \mathrm{SCN}^- & (2) \end{cases}$$

$k_{is} = 8 \times 10^{-5}$ s^{-1} and $k_{aq} = 1.7 \times 10^{-4}$ s^{-1} at 70 °C and I = 0.50 ($LiClO_4$)

$[Co(SCN)(edta)]^{2-}$ and $[Co(SCN)(Hedta)]^-$ (pK_a = 3.28 ± 0.02 at 20.0 °C and I = 1.0 (KCl)) liberated thiocyanate and changed to $[Co(edta)]^-$.

$$[\mathrm{Co(SCN)(edta)}]^{2-} \xrightarrow{k_1} [\mathrm{Co(edta)}]^- + \mathrm{SCN}^- \qquad (3)$$

$$[\mathrm{Co(SCN)(Hedta)}]^- \xrightarrow{k_2} [\mathrm{Co(edta)}]^- + \mathrm{H}^+ + \mathrm{SCN}^- \qquad (4)$$

$k_1 = 2.6 \times 10^{-4}$ s^{-1} and $k_2 = 1.2 \times 10^{-4}$ s^{-1} at 47.6 °C and I = 1.0 ($LiClO_4$)

A reaction analogous to Reaction 3 occurred even in the solid state. Infrared spectra of Ca[Co(SCN)(edta)] measured in a KBr disk indicated the following reaction :

$$\mathrm{Ca[Co(SCN)(edta)]} \longrightarrow \mathrm{Ca[Co(edta)](SCN)}$$

The rate of this reaction was much slower than that in aqueous solution.

No linkage isomerization of $[Co(SCN)(edta)]^{2-}$ was observed. This means that $[Co(NCS)(edta)]^{2-}$ formed in the reaction of $[Co(H_2O)(Hedta)]$ and SCN^- is not derived from $[Co(SCN)(edta)]^{2-}$, but from direct substitution of the aqua ligand in $[Co(H_2O)(Hedta)]$ by thiocyanate.[20)] Therefore, the over-all reaction sequence for the formation of $[Co(CNS)(Hedta)]^-$ can be expressed as follows :

$$\begin{tikzcd}
 & & {[Co(SCN)(Hedta)]^-} \arrow[dd, leftrightarrow, "\times" description] \\
{[Co(edta)]^-} \arrow[r, shift left, "+H_3O^+"] & {[Co(H_2O)(Hedta)]} \arrow[l, shift left, "-H_3O^+"] \arrow[ur, "+SCN^-"] \arrow[dr] & \\
 & & {[Co(NCS)(Hedta)]^-}
\end{tikzcd}$$

It was also found that, in neutral or acidic solutions, the direct substitution of $[Co(H_2O)(NH_3)_5]^{3+}$ with SCN^- gave both $[Co(SCN)(NH_3)_5]^{2+}$ and $[Co(NCS)(NH_3)_5]^{2+}$ simultaneously.[21)]

The simultaneous formation of the thiocyanato and isothiocyanato linkage isomers appears to be a more common phenomenon than has previously been appreciated for the reactions between SCN^- and cobalt(III) complexes containing one water molecule. In the reactions of cobalt(III) complexes containing more than one water molecule, more complicated linkage isomerism should be observed.

References

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8) CNS^- represents thiocyanate which does not specify the coordination mode.
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20) $[Co(CNS)(edta)]^{2-}$ is present as the equilibrium mixture of $[Co(CNS)(edta)]^{2-}$ and the corresponding conjugate acid form, $[Co(CNS)(Hedta)]^-$.
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