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The Syntheses and Properties of Mixed Cobalt(III) Complexes Containing 2-Mercaptoacetic Acid or 3-Mercaptopropionic Acid

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Synopsis. The following mixed cobalt(III) complexes were prepared and characterized: $[Co(SCH_2COO)en_2]X$ and $[Co(SCH_2CH_2COO)en_2]X$, where X is a chloride or iodide ion. Those complexes are common mononuclear complexes, in which the mercaptocarboxylic acids of the ligands function as bidentate ligands.

As a part of a series of the coordinating behavior of thiols in cobalt(III) complexes, mixed cobalt(III) complexes containing 2-aminoethanethiol$^{1)}$ or 2-mercaptoethanol$^{2)}$ have been reported. For those complexes, two type are found, one being mononuclear and the other binuclear; the coordinated thiolic sulfurs of the ligands are terminal and bridged respectively. This work was undertaken in order to prepare mixed cobalt(III) complexes containing 2-mercaptoacetic acid or 3-mercaptopropionic acid and to compare the results with the previous ones.

Experimental

Preparation. $[Co(SCH_2COO)en_2]X$ *(X is Cl or I)*: Twenty millilitters of an aqueous solution containing 0.9 g of 2-mercaptoacetic acid and 1.1 g of sodium hydroxide were stirred, drop by drop, into a solution of 2.8 g of *trans*-$[CoCl_2en_2]Cl$ in water (40 ml). The mixture was further stirred for 30 min and concentrated to half its volume *in vacuo*, and then we added 4 g of potassium iodide. On standing, a crude product of iodide was precipitated. Recrystallization was carried out from water.

Found: C, 18.64; H, 4.71; N, 14.35%. Calcd for $C_6H_{18}O_2N_4SICo$: C, 18.19; H, 4.59; N, 14.15%.

When the concentration of the starting solution was higher, $Na_3[Co_3(SCH_2COO)_6]^{3)}$ was also obtained.

The solution of the corresponding chloride was obtained from the solution of iodide by passing it over chloride-form anion-exchange resin. The solution was concentrated *in vacuo* and then cooled. The chloride thus precipitated was recrystallized from a small volume of water by adding ethanol.

Found: C, 24.18; H, 5.88; N, 18.11%. Calcd for $C_6H_{18}O_2N_4SClCo$: C, 24.64; H, 5.97; N, 18.39%. Absorption maxima, nm(log ε): 518(2.14), 382(shoulder) (2.4), and 282 (4.03).

$[Co(SCH_2CH_2COO)en_2]X$ *(X is Cl or I)*: These complexes were prepared by a method similar to that described above, except that 1.05 g of 3-mercaptopropionic acid were used instead of 2-mercaptoacetic acid.

Found (Iodide): C, 20.71; H, 5.31; N, 14.06%. Calcd for $C_7H_{20}O_2N_4SICo$: C, 20.49; H, 4.92; N, 13.66%. Found (Chloride): C, 26.25; H, 6.17; N, 17.33%. Calcd for $C_7H_{20}O_2N_4SClCo$: C, 26.37; H, 6.34; N, 17.58%. Absorption maxima, nm (log ε): 525(2.14), 385(shoulder) (2.4), and 291(4.10).

Apparatus. The same instruments as described previously were used.$^{2)}$

Results and Discussion

The absorption spectra of the complexes are shown in Fig. 1, together with those of the related complexes. The absorption spectra of the complexes are similar to that of $[Co(SCH_2CH_2NH_2)en_2]Cl_2$,$^{1)}$ but they are not similar to that of $[Co_2(SCH_2CH_2NH_2)_2dien_2]Cl_4$,$^{1)}$ which is a binuclear complex bridged by the thiolic sulfurs of ligands. The maximum values of the first absorption band for the present complexes and $[Co(SCH_2CH_2NH_2)en_2]Cl_2$ are regularly shifted to longer wavelengths in the order of the 2-aminoethanethiolato, 2-mercaptoacetate, and 3-mercaptopropionate complexes. The molar conductivities of the complexes show the values of 103—107 mho·cm^{-1}, indicating that they are 1: 1-type electrolytes. From all of these facts, it was concluded that the complexes have configurations similar to that of $[Co(SCH_2CH_2NH_2)en_2]Cl_2$, in which a thiolic sulfur of the ligand is combined with a cobalt(III) ion.

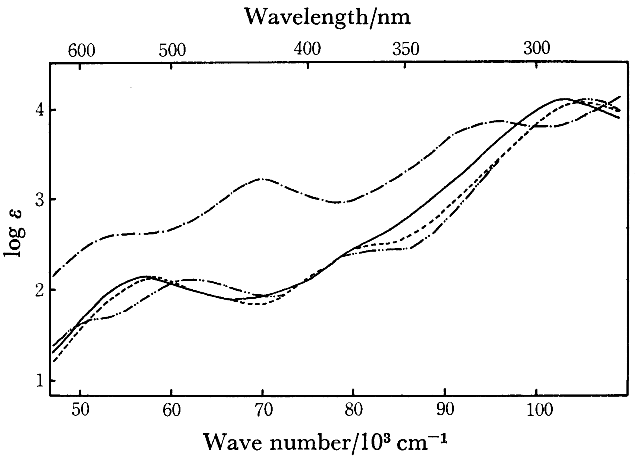

Fig. 1. Absorption spectra of the complexes.
—··—: $[Co(SCH_2CH_2NH_2)en_2]Cl_2$, ----: $[Co(SCH_2COO)en_2]Cl$, ——: $[Co(SCH_2CH_2COO)en_2]Cl$, —·—: $[Co_2(SCH_2CH_2NH_2)_2dien_2]Cl_4$.

The infrared spectral data of the complexes are summarized in Table 1, together with those of the related complexes. The assignments of the bands shown in the table were made tentatively by reference to the spectra of the related complexes. In all the complexes, the bands indicating the presence of the coordinated ethylenediamine and carboxylato groups are observed.$^{4,5)}$ No ν(S–H) band are observed in the 2500—2600 cm^{-1} region. From the infrared spectra it was also considered that the complexes have the configurations shown above. In $[Co(SCH_2CH_2COO)en_2]Cl$, the wave number of the ν_a(COO) band is higher than those of usual carboxylato

Table 1. The main bands of infrared spectra of the complexes (cm^{-1})

$[Co(SCH_2CH_2NH_2)en_2]Cl_2$	$[Co(SCH_2CH_2NH_2)en_2]Cl_2$-D[9]	$[Co(SCH_2COO)en_2]Cl$	$[Co(SCH_2COO)en_2]Cl$-D[9]	$[Co(SCH_2CH_2COO)en_2]Cl$	$[Co(SCH_2CH_2COO)en_2]Cl$-D[9]	$[Co(SCH_2CH_2COO)en_2]I$	$[Co(SCH_2CH_2COO)en_2]I$-D[9]	Tentative assignments
3370 (s)		3365 (s)		3340 (s)				ν(N–H)
3190 (s)		3220 (s)		3250 (s)		3230 (s)		
3120 (s)		3120 (s)		3200 (s)		3135 (s)		
	2380 (s)		2375 (s)	3120 (s)		3095 (s)		
	2265 (s)		2280 (s)		2380 (s)		2410 (s)	ν(N–D)
		1618 (s)	1594 (s)		2280 (s)		2290 (s)	
1576 (s)		1562 (s)		1682 (m)	1580 (s)	1610 (s)	1578 (s)	ν_a(COO)
		1350 (s)	1340 (s)	1563 (s)		1552 (s)		δ(N–H)
	1162 (s)		1175 (s)	1394 (s)	1380 (s)	1377 (s)	1378 (s)	ν_s(COO)
515 (sh)	467 (m)	504 (w)	470 (sh)		1150 (s)		1158 (s)	δ(N–D)
496 (m)	455 (w)	494 (m)		500 (m)	470 (m)	513 (w)	475 (m)	ν(Co–N)
		370 (m)	365 (m)	495 (m)		500 (m)	465 (sh)	
326 (m)	327 (w)	310 (w)	308 (w)	346 (m)	340 (m)	342 (m)	340 (m)	ν(Co–O)
				300 (w)	295 (sh)	298 (m)	298 (m)	ν(Co–S)

Abbreviation; s: strong, m: medium, w: weak, sh: shoulder.

complexes. It was assumed, comparing the spectra of the chloride and the related complexes and considering the deuterated effects, that the shift in the chloride is due to the intramolecular hydrogen bond. The ν(Co–N) and ν(Co–O) bands of the complexes were assigned by considerations similar to that of the cobalt(III) complexeswith (2-aminoethylthio) acetic acid.[6] The ν(Co–S) band for the present cobalt(III) complexes is expected, from the bands assignments of the related complexes,[7] to appear in the 280—370 cm^{-1} region. Therefore, among the bands appearing in those region for the complexes we selected the corresponding bands, considering the effects due to deuterations.

The complexes are changed by the reactions with alkyl halides to $[Co(R\text{-}SCH_2COO)en_2]X_2$ or $[Co(R\text{-}SCH_2CH_2COO)en_2]X_2$, in which the coordinated thiolic sulfurs are alkylated like $[Co(SCH_2CH_2NH_2)en_2]Cl_2$.[8]

References

1) K. Hori, *Nippon Kagaku Zasshi*, **90**, 561 (1969).

2) K. Hori, *ibid.*, **91**, 547 (1970).

3) K. Hori, *ibid.*, **92**, 322 (1971).

4) M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369; N. Sato and J. Fujita, *Spectrochim. Acta*, **22**, 577 (1966).

5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, (1970), p. 222.

6) K. Hori, unpublished work.

7) G. W. Watt, J. F. Knifton, and C. V. Senoff, *Inorg. Chem.*, **8**, 2252 (1969).

8) K. Hori, *Bull. Yamagata Univ. (Nat. Sci.)*, **8**, 403 (1974).

9) They represent the complexes in which the amino groups of the ligands in the corresponding complexes were deuterated.