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Preparation and Properties of Cobalt(II) and -(III) Complexes of (2-Aminoethylthio)acetic Acid

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Synopsis. The cobalt(II) and -(III) complexes of (2-aminoethylthio)acetic acid (HL), $[CoL_2]\cdot H_2O$, *trans*-(*N*)-$[CoL_2]Cl$ and *cis*(*N*)-$[CoL_2]Cl\cdot 2H_2O$ were prepared and characterized. These complexes are octahedral in which the ligand is coordinated through the N, S and O atoms as a terdentate ligand.

As a part of a study on the cobalt(III) complexes containing sulfides as a ligand, the complexes of bis(2-aminoethyl)sulfide[1] and 2,2′-thiodiacetic acid[2] have been reported. For the former ligand, only tri-valent complexes were obtained, while for the latter, di-valent complexes were generally obtained. This work was undertaken to prepare cobalt(III) complexes of (2-aminoethylthio)acetic acid and to compare the results with the previous ones.

Experimental

Preparation. *Bis[(2-aminoethylthio)acetato]cobalt(II) monohydrate,* $[Co(NH_2CH_2CH_2SCH_2COO)_2]\cdot H_2O$ *(1).* A solution of 4.05 g (0.03 mol) of (2-aminoethylthio)acetic acid in 50 ml of water was adjusted to about pH 11.5 with a sodium hydroxide solution. 2.67 g (0.01 mol) of hexaamminecobalt(III) chloride was added to the solution. The solution was heated at 70—75 °C until ammonia gas evolution ceased, and was filtered. On standing, pinkish crystals were precipitated. Recrystallization was carried out from water.

Found: C, 27.67; H, 5.02; N, 8.06; Co, 17.02%. Calcd for $C_8H_{18}O_5N_2Co$: C, 27.82; H, 5.26; N, 8.11; Co, 17.06%.

trans(N)- *and* cis(N)-*bis[(2-aminoethylthio)acetato]cobalt(III) chloride,* trans(N)-$[Co(NH_2CH_2CH_2SCH_2COO)_2]Cl$ *(2) and* cis(N)-$[Co(NH_2CH_2CH_2SCH_2COO)_2]Cl\cdot 2H_2O$ *(3).* To an aqueous solution of 3.37 g (0.025 mol) of (2-aminoethylthio)acetic acid adjusted to about pH 9 was added 2.38 g (0.01 mol) of cobalt(II) chloride hexahydrate. The solution was gradually concentrated at 70 °C until it became sticky. Adding 2 ml of 30% hydrogen peroxide, the color of the solution turned to red-purple. The solution was allowed to stand for several days to precipitate the mixture of complexes **2** and **3**. In order to separate the two complexes, a part of the mixture was dissolved in a small volume of warm water and filtered. When the filtrate was cooled, purple crystals of complex **3** were precipitated. The remaining portion of the mixture was dissolved in warm water, and the same volume of ethanol was added. On cooling, red-purple crystals of complex **2** were precipitated. Both of the complexes **2** and **3** were recrystallized from a small amount of water by adding ethanol.

Found for (**2**): C, 26.52; H, 4.64; N, 7.83; Co, 15.67%. Calcd for $C_8H_{16}O_4N_2S_2ClCo$: C, 26.49; H, 4.45; N, 7.72; Co, 16.24%. Found for (**3**): C, 24.05; H, 5.39; N, 7.11; Co, 14.75%. Calcd for $C_8H_{20}O_6N_2S_2ClCo$: C, 24.09; H, 5.06; N, 7.03; Co, 14.78%.

Apparatus. The same instruments as those described previously were used.[1,2]

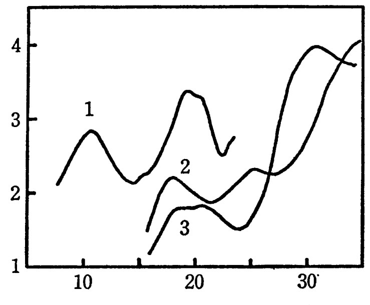

Fig. 1. Electronic spectra of complexes.
1: Reflection spectrm of (**1**) (arbitrary scale), 2: Absorption spectrum of (**2**), 3: Absorption spectrum of (**3**).

Results and Discussion

The reflectance spectrum of complex **1** is similar to those of well-known octahedral cobalt(II) complexes such as $[Co(H_2O)_6]^{2+}$ in the near-infrared and visible regions (Fig. 1).[3] Furthermore, the magnetic moment value of 5.18 B.M. obtained falls within the range of 4.7—5.2 B.M. usually found for regular high-spin octahedral complexes.[4] Therefore, complex **1** is concluded to be a high-spin octahedral cobalt(II) complex.

From the infrared spectral data, it is proven directly that both amino and carboxylate groups are coordinated in the ligand. When the S atom with both N and O terminals is present in a straight chain ligand molecule around the central cobalt(II) ion, it will be useful to promote the coordinating effect of the sulfur. Finally, since all N, O and S atoms in the ligand can be coordinated potentially on chelation, it seems more practical to consider the existence of a terdentate ligand in this case.

On the other hand, both complexes **2** and **3** are diamagnetic and their molar extinction coefficients are appropriate for the cobalt(III) complexes (Fig. 1). Therefore, they are concluded to be octahedral cobalt(III) complexes. The ligand in these complexes is concluded to function as a terdentate ligand from a consideration analogous to the case of complex **1**.

The absorption spectrum of complex **2** shows a splitting in the first band while that of complex **3** does not. The patterns of the absorption spectra of complexes **2** and **3** are similar to those of *trans*- and *cis*-$K[Co(ida)_2]$,[5] respectively, in the visible region. Such a similarity indicates that these complexes of the $N_2S_2O_2$ type may be similar to cobalt(III) complexes of iminoacetic acid of the N_2O_4 type in the strength of crystal field splitting. It is, therefore, suggested that complex **2** which has a splitting in the first band is the

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

(**1**)	NiL$_2$[a]	CuL$_2$[a]	(**2**)	(**3**)	Complex
3248(s)	3260(s)	3220(s)	3200(s)	3270(s)	ν(N-H)
3140(s)	3130(s)	3120(s)	3080(s)	3220(m) 3200(m)	
1630(s)	1636(s)	1628(s)	1630(s)	1638(s)	ν_a(COO)
1565(s)	1570(s)	1570(s)	1586(s)	1563(s)	δ(N-H)
1366(s)	1368(s)	1365(s)	1318(s)	1320(s)	ν_s(COO)
370(m)	381(m)	418(m)	537(m)	528(m)	ν(M-N)
265(m)	278(m)	340(w)	374(m)	375(m)	ν(M-O)
240(w)	254(w)	260(w)	270(w)	265(w)	ν(M-S)

a) L=$NH_2CH_2CH_2SCH_2COO^-$. s: strong, m: medium, w: weak.

trans form with respect to the nitrogen atoms and complex **3** which shows no splitting is the *cis* form, as in the case of K[Co(ida)$_2$]. For these cobalt(III) complexes, six geometrical forms are possible: two species with a *trans*(*N*)-*fac* configuration, one with a *cis*(*N*)-*mer* configuration and three with a *cis*(*N*)-*fac* configuration. However, the detailed coordination structures is not known because no NMR data are available, owing to the poor solubility of the complexes. Considering the reduced yield of the *mer* configuration in the complexes with iminodiacetic acid or the related ligand,[5,6] the *mer* configuration does not seem to be contained in these complexes.

The infrared spectral data of the complexes are summerized in Table 1, together with those of nickel(II) and copper(II) complexes of (2-aminoethylthio)-acetic acid. The assignments of the bands are tentative and were made with reference to the spectra of related complexes,[7] considering deuteration effects. The ν(Co(III)–N) bands for complexes **2** and **3** were assigned to slightly higher wave numbers, because no corresponding bands could be found the bands appearing in the 480—520 cm^{-1} region. In the complexes containing the bond of thioether-type sulfur and metal, the ν(M–S) bands have been assigned to the 210—260 cm^{-1} region for the cobalt(II), nickel(II) and copper(II) complexes with (alkylthio)acetic acid,[8] and to 307 and 316 cm^{-1} for the palladium(II) and platinum(II) complexes with dimethyl sulfide, respectively.[9] It was therefore expected that the ν(Co(II)–S) and ν(Co(III)–S) bands for the present complexes would appear in the 210—250 cm^{-1} and 250—300 cm^{-1} regions, respectively. The appropriate bands appearing in this region and corresponding to the nickel and copper complexes shown in Table 1 are unique for each of the complexes **1**, **2** and **3**. These were assigned to the ν(Co(II)–S) and ν(Co(III)–S) bands, respectively.

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