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Structural Studies of Thiocyanato and Isothiocyanato Cobalt(III) Complexes Ligating Diamine-*N*,*N′*-polycarboxylates

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Crystal and molecular structures of $NH_4[Co(NCS)(hedtra)]\cdot H_2O$ and $K[Co(SCN)(edtra)]\cdot 1.5H_2O$ have been determined by single-crystal X-ray analyses, where hedtra^{3-} and edtra^{3-} denote *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetate and ethylenediamine-*N*,*N*,*N′*-triacetate ions, respectively. Crystal data are as follows: For the former species, triclinic, space group P1, a=7.477(2)Å, b=9.135(2)Å, c=6.899(1)Å; α=84.37(2)°, β=107.31(2)°, γ=108.35(2)°, V=427.0(2)Å^3, Z=1; for the latter species, monoclinic, space group P2$_1$/a, a=15.288(2)Å, b=7.059(1)Å, c=14.373(2)Å, β=107.55(1)°, V=1479.0(4)Å^3, Z=4. It has been proved unequivocally that the former species contains N-bonded SCN^- ligand and the latter species, the S-bonded ligand. Coordination geometry around the cobalt atom in each species deviates considerably from the regular octahedron, so that a very open space is created around the Co–NCS or Co–SCN moiety. This structural feature may be associated with the facile formation of the novel S-bonded species.

Quite recently, a pair of linkage isomers, $[Co(NCS)L]^{n-}$ and $[Co(SCN)L]^{n-}$, were prepared, where L denotes ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate ion (edta^{4-}) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetate ion (hedtra^{3-}); n is 2 for edta^{4-} and 1 for hedtra^{3-}.[1] When $[Co(hedtra)(H_2O)]$ is allowed to react with SCN^-, comparable amounts of both $[Co(SCN)(hedtra)]^-$ and $[Co(NCS)(hedtra)]^-$ are formed simultaneously in an early stage of the reaction. Then, the thiocyanato (S-bonded) isomer changes to the isothiocyanato (N-bonded) isomer, because the N-bonded isomer is thermodynamically more stable than the S-bonded isomer. Therefore, the novel S-bonded isomer can be obtained in a good yield by controlling the reaction time.

Although the simultaneous formation of both $[Co(SCN)(NH_3)_5]^{2+}$ and $[Co(NCS)(NH_3)_5]^{2+}$ was also observed by the direct reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ with SCN^-, the yield of the S-bonded isomer was much lower than that of the N-bonded isomer.[1] In the reaction of $[Co(CN)_5(H_2O)]^{2-}$ with SCN^-, the initial product has been found to be the N-bonded isomer $[Co(CN)_5(NCS)]^{3-}$.[2] Therefore, in the systems of $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(CN)_5(H_2O)]^{2-}$, the N-bonded isomers are formed more easily than the S-bonded isomers. In order to elucidate the reason why $[Co(SCN)(hedtra)]^-$ is formed in a good yield, X-ray structural studies were undertaken for single crystals of $K[Co(SCN)(edtra)]\cdot 1.5H_2O$ and $NH_4[Co(NCS)(hedtra)]\cdot H_2O$, where edtra^{3-} denotes ethylenediamine-*N*,*N*,*N′*-triacetate ion.

Experimental

Materials. Ammonium salt of the complex, $NH_4[Co(NCS)(hedtra)]\cdot H_2O$, was prepared from the corresponding potassium salt $K[Co(NCS)(hedtra)]\cdot 2.5H_2O$[1] by use of ion-exchange resin (QAE Sephadex). Slow evaporation of an aqueous solution saturated with the ammonium salt gave reddish violet needle crystals of $NH_4[Co(NCS)(hedtra)]\cdot H_2O$. Found: C, 30.74; H, 4.90; N, 13.10%. Calcd for $NH_4[Co(NCS)(hedtra)]\cdot H_2O$: C, 30.85; H, 4.94; N, 13.08%.

Potassium salt of the complex, $K[Co(SCN)(edtra)]\cdot 1.5H_2O$, was prepared by a method similar to $NH_4[Co(SCN)(hedtra)]\cdot 0.3H_2O$.[1] Found: C, 26.09; H, 3.41; N, 10.29%. Calcd for $K[Co(SCN)(edtra)]\cdot 1.5H_2O$: C, 26.74; H, 3.71; N, 10.14%. Blue plate crystals of $K[Co(SCN)(edtra)]\cdot 1.5H_2O$ were obtained by dropwise addition of 0.3 ml of methanol to an aqueous solution of the complex (10 mg of complex in 6 ml of water) and by leaving the solution in a refrigerator for two weeks.

X-Ray Analyses. Diffraction data were obtained on a Rigaku automated four circle diffractometer AFC-5 with graphite monochromatized Mo$K\alpha$ radiation (λ=0.71073 Å). Intensity data were corrected for the Lorentz-polarization effects and for absorption. The lattice parameters were obtained from the least-squares fit of 50 (for $NH_4[Co(NCS)(hedtra)]\cdot H_2O$) and 35 (for $K[Co(SCN)(edtra)]\cdot 1.5H_2O$) 2θ values with $25° < 2\theta < 30°$.

The structures of both complexes were solved by standard heavy-atom techniques and refined by block-diagonal least square methods. The weight (w) was taken as $w=[\sigma_c^2+(0.015|F_o|)^2]^{-1}$. The scattering factors for non-hydrogen atoms were taken from the literatures.[3] For hydrogen, the values given by Stewart *et al.* were used.[4] All the hydrogen atoms were located by difference syntheses and included in the refinement with isotropic temperature factors. Absolute configuration of the $NH_4[Co(NCS)(hedtra)]\cdot H_2O$ was determined by using anomalous scattering technique. Least-squares calculation including the anomalous scattering corrections for non-hydrogen atoms gave R and R_w values of 0.023 and 0.029. The enantiomeric structure was refined under identical conditions to give R and R_w values of 0.032 and 0.045, respectively. The crystal specimen of $NH_4[Co(NCS)(hedtra)]\cdot H_2O$ used in the X-ray work has the absolute configuration illustrated in Fig. 1 ($\Lambda(R,R)\Delta(R,G)$ form, *vide infra*). When the R-factor ratio test[5] was applied to the R_w values, the alternative model was rejected at the less than 0.005 significant level. Crystallographic data and the final R indices are summarized in Table 1. The final fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms of NH_4[Co-

TABLE 1. CRYSTALLOGRAPHIC PARAMETERS

	$NH_4[Co(NCS)(hedtra)]\cdot H_2O$	$K[Co(SCN)(edtra)]\cdot 1.5H_2O$
Formula	$CoSC_{11}H_{19}N_4O_7\cdot H_2O$	$KCoSC_9H_{11}N_3O_6\cdot 1.5H_2O$
Crystal system	Triclinic	Monoclinic
Space group	P1	$P2_1/a$
a/Å	7.477(2)	15.288(2)
b/Å	9.135(2)	7.059(1)
c/Å	6.899(1)	14.373(2)
α/deg	84.37(2)	—
β/deg	107.31(2)	107.55(1)
γ/deg	108.35(2)	—
V/Å^3	427.0(2)	1479.0(4)
Z	1	4
d_c/g cm^{-3}	1.67	1.86
d_m/g cm^{-3}	1.67	1.83
Crystal size/mm	0.56×0.16×0.14	0.4×0.4×0.3
Scan range/degree	$1.3+0.5\tan\theta$	$1.2+0.5\tan\theta$
Scan mode	θ—2θ	θ—2θ
$2\theta_{max}$/deg	55	55
μ/mm^{-1}	1.21	1.65
Unique reflections	2322	3822
Observed reflections[a]	2039	3086
R	0.023	0.029
R_w	0.029	0.038

a) $|F_o|>3\sigma(|F_o|)$.

TABLE 2. FRACTIONAL COORDINATES (×10^4) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR NON-HYDROGEN ATOMS OF $NH_4[Co(NCS)(hedtra)]\cdot H_2O$

Atom	x	y	z	B_{eq}
Co	5000(1)	5000(1)	5000(1)	1.5
S	1808(1)	8695(1)	4216(2)	3.8
O(1)	4606(3)	3815(2)	7375(3)	2.2
O(2)	4779(3)	1591(3)	8917(4)	2.7
O(3)	7155(3)	6511(2)	6588(3)	2.1
O(4)	10197(3)	6896(3)	8566(4)	3.4
O(5)	2865(3)	3439(2)	3443(3)	2.1
O(6)	797(4)	2945(3)	366(4)	3.6
O(7)	7349(3)	9904(2)	494(4)	2.9
N(1)	6805(3)	3839(2)	5106(4)	1.7
N(2)	5399(3)	5916(2)	2378(4)	1.5
N(NCS)	3314(4)	6206(3)	5039(4)	2.3
C(1)	6829(4)	3746(3)	2957(4)	2.0
C(2)	6959(4)	5332(3)	2037(4)	1.9
C(3)	5978(5)	2308(3)	5996(5)	2.2
C(4)	5067(4)	2557(3)	7585(5)	2.0
C(5)	8769(4)	4671(3)	6439(5)	2.1
C(6)	8739(4)	6140(3)	7282(5)	2.0
C(7)	3465(4)	5286(3)	843(5)	2.0
C(8)	2250(4)	3768(3)	1536(5)	2.1
C(9)	6061(4)	7644(3)	2296(5)	2.1
C(10)	6310(5)	8302(4)	258(5)	2.9
C(NCS)	2708(4)	7250(3)	4710(5)	2.2
N(a)	589(4)	10070(3)	8557(5)	3.1
O(w)	9560(4)	1333(3)	−5447(4)	3.3

TABLE 3. FRACTIONAL COORDINATES (×10^4) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR NON-HYDROGEN ATOMS OF $K[Co(SCN)(edtra)]\cdot 1.5H_2O$

Atom	x	y	z	B_{eq}
K	1672(1)	−3076(1)	9593(1)	4.5
Co	184(1)	288(1)	6888(1)	1.7
S	1519(1)	−798(1)	6663(1)	2.9
O(1)	163(1)	−1596(3)	7840(1)	2.7
O(2)	−325(1)	−1947(4)	9139(2)	4.6
O(3)	−447(1)	−1295(2)	5832(1)	2.3
O(4)	−1812(1)	−2607(3)	5143(2)	3.5
O(5)	810(1)	1950(3)	7903(1)	2.5
O(6)	1734(2)	4448(3)	8178(2)	4.7
N(1)	−1007(1)	988(3)	7021(1)	2.1
N(2)	105(1)	2467(3)	6033(1)	2.2
N(SCN)	2827(2)	−294(6)	8501(2)	6.5
C(1)	−1164(2)	3006(4)	6710(2)	2.7
C(2)	−856(2)	3207(4)	5805(2)	2.8
C(3)	−929(2)	635(4)	8062(2)	2.8
C(4)	−333(2)	−1109(4)	8383(2)	2.9
C(5)	−1706(2)	−305(4)	6376(2)	2.6
C(6)	−1315(2)	−1505(4)	5729(2)	2.3
C(7)	822(2)	3844(4)	6547(2)	3.0
C(8)	1162(2)	3438(4)	7629(2)	2.9
C(SCN)	2279(2)	−505(5)	7759(2)	3.6
O(w1)	1560(1)	790(3)	9863(1)	4.1
O(w2)	−52(5)	−4433(9)	10598(5)	9.0

(NCS)(hedtra)]·H_2O and K[Co(SCN)(edtra)]·$1.5H_2O$ are given in Tables 2 and 3.

All calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III.[6] The lists of structure factors and anisotropic thermal parameters are deposited at the Office of the Chemical Society of Japan (Document No. 8553).

Results and Discussion

Description of the Molecular Structures of [Co(NCS)(hedtra)]$^-$ and [Co(SCN)(edtra)]$^-$. Figures 1 and 2 show, respectively, stereoscopic views of the complex anions, [Co(NCS)(hedtra)]$^-$ and [Co(SCN)(edtra)]$^-$.

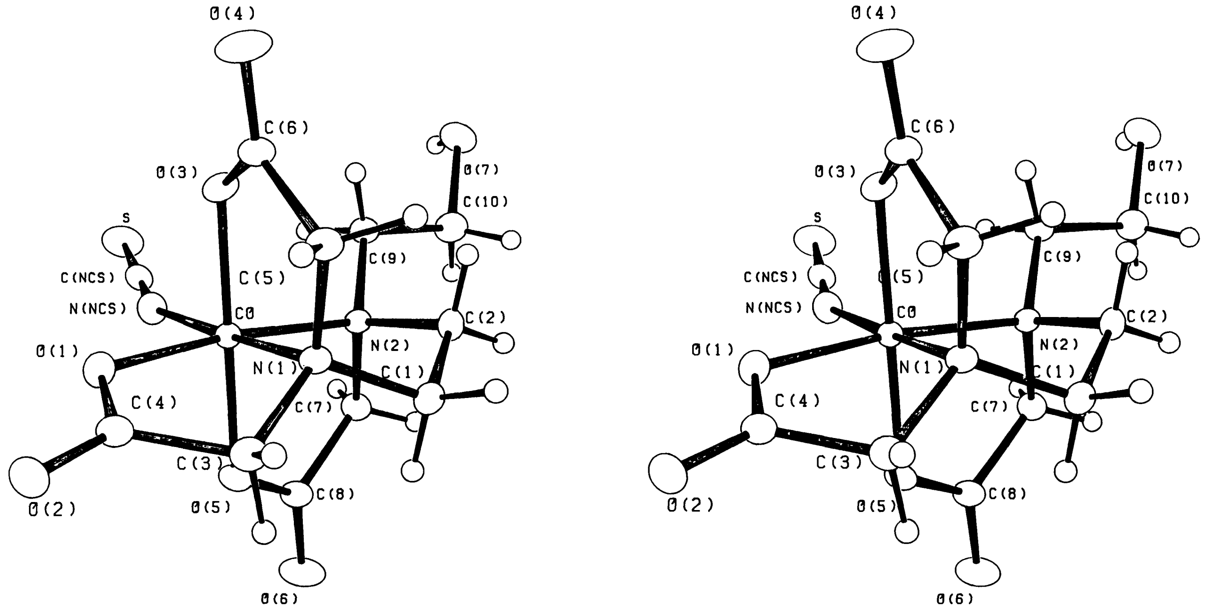

Fig. 1. Stereoscopic view of [Co(NCS)(hedtra)]$^-$.

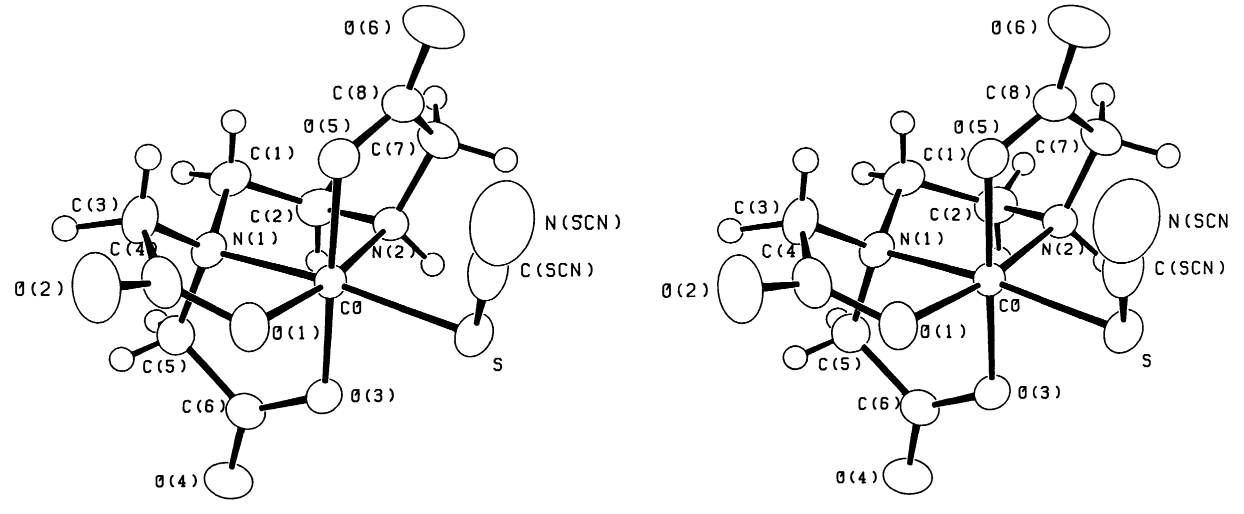

Fig. 2. Stereoscopic view of [Co(SCN)(edtra)]$^-$.

The relevant bond lengths and bond angles based on the atomic numbering scheme in these figures are listed in Tables 4—7. The present structural determinations prove unequivocally that [Co(NCS)(hedtra)]$^-$ contains isothiocyanato ligand and [Co(SCN)(edtra)]$^-$, thiocyanato ligand. The diamine-*N*,*N'*-polycarboxylate ions, hedtra^{3-} and edtra^{3-}, act as pentadentate ligands. In each complex, isothiocyanato or thiocyanato ligand exists in the plane containing cobalt atom and two amino nitrogen atoms. Wiekliem and Hoard have pointed out for [Co(edta)]$^-$ that the strain in the complex can be expressed by the deviation from planarity of acetate (N-C-C-O-Co) rings.[7] The out-of-plane acetate rings (*R* rings) of the complexes studied here are less strained than the in-plane acetate rings (*G* rings), because the deviation from the planality of the *R* rings is smaller than that of the *G* rings. Similar trends have been observed for other related complexes, [Co(Hedta)(H$_2$O)][8] and [Co(NO$_2$)(edtra)]$^-$.[9] The strains existing in the complexes are also disclosed in the Co-O bond lengths: The Co-O bond lengths of the *G* rings are longer than those of the *R* rings.

The bond angle of Co-N(NCS)-C(NCS) in [Co(NCS)(hedtra)]$^-$ is 157.1(3)°. This value deviates significantly from the values commonly found for various N-bonded complexes. The reported values lie in the range of 163.5—177.6°.[10—14] The deviation may come from a packing effect, because any specific group which can interact with the Co-NCS group is absent. The value of the bond angle of Co-S(SCN)-C(SCN) in [Co(SCN)(edtra)]$^-$ (102.9(1)°) is within the range of

Table 4. Bond lengths (l/Å) for $NH_4[Co(NCS)(hedtra)]\cdot H_2O$

Co-O1	1.918(2)	Co-O3	1.883(2)
Co-O5	1.893(2)	Co-N1	1.944(3)
Co-N2	1.982(2)	Co-N(NCS)	1.924(3)
S-C(NCS)	1.626(4)	O1-C4	1.284(4)
O2-C4	1.228(4)	O3-C6	1.277(4)
O4-C6	1.233(3)	O5-C8	1.296(4)
O6-C8	1.216(3)	O7-C10	1.424(4)
N1-C1	1.498(4)	N1-C3	1.492(3)
N1-C5	1.487(3)	N2-C2	1.510(4)
N2-C7	1.493(3)	N2-C9	1.499(3)
N(NCS)-C(NCS)	1.156(4)	C1-C2	1.510(4)
C3-C4	1.519(5)	C5-C6	1.522(5)
C7-C8	1.519(4)	C9-C10	1.513(5)

Table 5. Bond angles (degree) for $NH_4[Co(NCS)(hedtra)]\cdot H_2O$

O1-Co-O3	91.3(1)	O1-Co-O5	87.7(1)
O1-Co-N1	83.8(1)	O1-Co-N2	171.0(1)
O1-Co-N(NCS)	94.8(1)	O3-Co-O5	178.4(1)
O3-Co-N1	87.4(1)	O3-Co-N2	94.4(1)
O3-Co-N(NCS)	89.6(1)	O5-Co-N1	91.2(1)
O5-Co-N2	86.5(1)	O5-Co-N(NCS)	91.7(1)
N1-Co-N2	89.4(1)	N1-Co-N(NCS)	176.7(1)
N2-Co-N(NCS)	92.3(1)	Co-O1-C4	114.8(2)
Co-O3-C6	115.5(2)	Co-O5-C8	115.2(2)
Co-N1-C1	105.9(2)	Co-N1-C3	105.5(2)
Co-N1-C5	108.5(2)	C1-N1-C3	113.4(2)
C1-N1-C5	112.2(2)	C3-N1-C5	110.9(2)
Co-N2-C2	105.4(2)	Co-N2-C7	105.0(2)
Co-N2-C9	115.5(2)	C2-N2-C7	111.5(2)
C2-N2-C9	108.8(2)	C7-N2-C9	110.6(2)
Co-N(NCS)-C(NCS)	157.1(3)	N1-C1-C2	106.8(2)
N2-C2-C1	110.5(2)	N1-C3-C4	108.2(3)
O1-C4-O2	124.4(3)	O1-C4-C3	114.7(3)
O2-C4-C3	121.0(3)	N1-C5-C6	111.3(3)
O3-C6-O4	123.8(3)	O3-C6-C5	113.4(2)
O4-C6-C5	119.9(3)	N2-C7-C8	111.9(2)
O5-C8-O6	123.3(3)	O5-C8-C7	115.2(2)
O6-C8-C7	121.5(3)	N2-C9-C10	114.0(3)
O7-C10-C9	108.5(3)	S-C(NCS)-N(NCS)	178.7(2)

those reported for various S-bonded complexes (90—109°).[12,15]

The C-N (SCN) bond length of $[Co(NCS)(hedtra)]^-$ (1.156(4) Å) is essentially identical with those of $[Co(SCN)(edtra)]^-$ (1.150(5) Å), other cobalt(III) complexes containing thiocyanate ion such as $[Co(SCN)(NH_3)_5]^{2+}$ (1.14(4) Å)[15] and $[(CN)_5Co(SCN)Co(NH_3)_5]$ (1.145(7) Å)[12] and uncoordinated thiocyanate ion (1.158(5) Å and 1.149(7) Å).[16] Therefore, the C-N bond lengths of thiocyanate ion are hardly influenced by the bonding mode of thiocyanate ion. The C-S bond lengths, however, are influenced by the bonding mode: 1.664(3) Å for $[Co(SCN)(edtra)]^-$, 1.627(4) Å for $[Co(NCS)(hedtra)]^-$, 1.645(5) Å for $[(CN)_5Co(SCN)Co(NH_3)_5]$,[12] and 1.644(4) and 1.646(5) Å for free thiocyanate ion.[16] The C-S bond lengths change in the following order: Co-NCS$<$SCN$^-$$\simeq$Co-SCN-Co$<$Co-SCN.

Table 6. Bond lengths (l/Å) for $K[Co(SCN)(edtra)]\cdot 1.5H_2O$

Co-O1	1.915(2)	Co-O3	1.897(2)
Co-O5	1.892(2)	Co-N1	1.952(2)
Co-N2	1.949(2)	Co-S	2.292(1)
S-C(SCN)	1.664(3)	O1-C4	1.288(4)
O2-C4	1.233(4)	O3-C6	1.299(3)
O4-C6	1.227(3)	O5-C8	1.295(3)
O6-C8	1.216(4)	N1-C1	1.490(4)
N1-C3	1.486(4)	N1-C5	1.495(3)
N2-C2	1.500(3)	N2-C7	1.485(4)
N(SCN)-C(SCN)	1.150(5)	C1-C2	1.518(4)
C3-C4	1.519(4)	C5-C6	1.508(4)
C7-C8	1.511(4)		

Table 7. Bond angles (degree) for $K[Co(SCN)(edtra)]\cdot 1.5H_2O$

O1-Co-O3	92.8(1)	O1-Co-O5	89.6(1)
O1-Co-N1	83.6(1)	O1-Co-N2	170.7(1)
O1-Co-S	94.4(1)	O3-Co-O5	177.6(1)
O3-Co-N1	87.9(1)	O3-Co-N2	92.4(1)
O3-Co-S	87.1(1)	O5-Co-N1	92.1(1)
O5-Co-N2	85.3(1)	O5-Co-S	92.9(1)
N1-Co-N2	88.8(1)	N1-Co-S	174.5(1)
N2-Co-S	93.7(1)	Co-O1-C4	112.8(2)
Co-O3-C6	114.5(2)	Co-O5-C8	115.4(2)
Co-N1-C1	106.5(2)	Co-N1-C3	105.2(2)
Co-N1-C5	107.3(2)	C1-N1-C3	114.8(2)
C1-N1-C5	112.2(2)	C3-N1-C5	110.3(2)
Co-N2-C2	106.4(2)	Co-N2-C7	107.9(2)
C2-N2-C7	114.1(2)	Co-S-C(SCN)	102.9(1)
N1-C1-C2	106.5(2)	N2-C2-C1	108.5(2)
N1-C3-C4	107.5(2)	O1-C4-O2	123.7(3)
O1-C4-C3	116.2(3)	O2-C4-C3	120.1(3)
N1-C5-C6	112.5(2)	O3-C6-O4	123.4(2)
O3-C6-C5	116.5(2)	O4-C6-C5	120.0(2)
N2-C7-C8	111.2(2)	O5-C8-O6	124.2(3)
O5-C8-O7	115.0(3)	O6-C8-C7	121.5(3)
S-C(SCN)-N(SCN)	178.7(2)		

Infrared spectroscopy has been used for the determination of the bonding mode of thiocyanate ion.[17] The C-S stretching frequencies change in the order M-SCN$<$SCN$^-$$<$M-NCS and provide a good diagnostic test for the bonding mode.[18] The order is consistent with the change in the bond lengths shown above. Although it has been stated that the C-N stretching frequencies are generally higher for M-SCN than for M-NCS, the reverse is also sometimes true.[19] This comes from the fact that the C-N bond length is almost constant regardless of the bonding mode.

Description of the Crystal Structures of $NH_4[Co(NCS)(hedtra)]\cdot H_2O$ and $K[Co(SCN)(edtra)]\cdot 1.5H_2O$. The stereoscopic view of the crystal structure for $NH_4[Co(NCS)(hedtra)]\cdot H_2O$ is given in Fig. 3. The crystals of the compound belong to the space group P1 with one molecule in a unit cell as shown in Table 1. This necessitates the occurrence of a spontaneous resolution. This was confirmed by the measurement of the CD spectrum of the solution which was prepared by dissolving a single crystal in water. The absolute

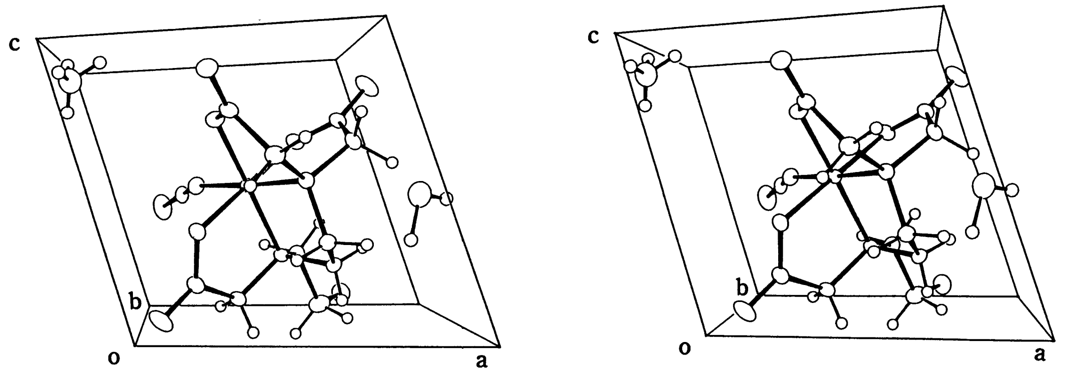

Fig. 3. Stereoscopic view of $NH_4[Co(NCS)(hedtra)]\cdot H_2O$.

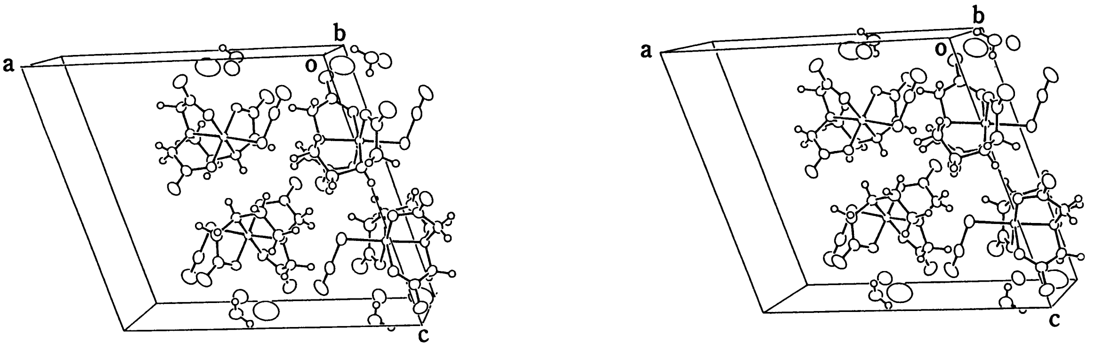

Fig. 4. Stereoscopic view of $K[Co(SCN)(edtra)]\cdot 1.5H_2O$.

configuration of the complex in the crystal used for X-ray analysis was $\Lambda(R,R)\Delta(R,G)$, showing that two R rings take Λ configuration and that one R ring (N2-C7-C8-O5-Co) and G ring take Δ configuration.

The stereoscopic view of the crystal structure for $K[Co(SCN)(edtra)]\cdot 1.5H_2O$ is given in Fig. 4. A unit cell of the complex is composed of four molecules which are two pairs of enantiomers, thus forming a racemic crystal.

Steric Circumstances around Cobalt(III) Centers in Thiocyanato and Isothiocyanato Cobalt(III) Complexes. The complexes, $[Co(NCS)(hedtra)]^-$ and $[Co(SCN)(edtra)]^-$, are so distorted that large open spaces are created around the coordination sites of N-bonded and S-bonded thiocyanate ions. This is evidenced by the fact that an angle of O(1)–Co–N(2) at the same side as NCS^- (or SCN^-) is opened to 189.0(1)° in $[Co(NCS)(hedtra)]^-$ and to 189.3(1)° in $[Co(SCN)(edtra)]^-$. We have attempted to evaluate the magnitude of the open spaces of these and the related complexes: The R_v value defined in Eq. 1 was calculated.

$$R_v = \sum_{cis} V_{do} / \sum_{cis} V_{ro} \qquad (1)$$

For a thiocyanato or an isothiocyanato complex, let us consider the plane which is perpendicular to the Co–SCN (or NCS) bond axis and involves the center of the cobalt atom (Fig. 5). The plane will hereafter be referred to as the cis plane. If the geometry of the complex is a regular octahedron, the centers of four donor atoms in cis position (A_1, A_2, A_3, and A_4) must be involved in the cis plane. In an actual complex, however, the four donor atoms deviate more or less from the cis plane. The space occupied by a cis donor atom is divided into two parts by the cis plane. The quantity given in Eq. 1, V_{do}, denotes the volume of the part of the side containing the thiocyanato ligand. Hence the term $\sum_{cis} V_{do}$ denotes the sum of the V_{do} values of the four atoms in the cis plane. The V_{ro} value is defined as the V_{do} value obtained when the geometry of the complex is assumed to be a regular octahedron. According to the definition, $\sum_{cis} V_{ro}$ can be expressed as follows:

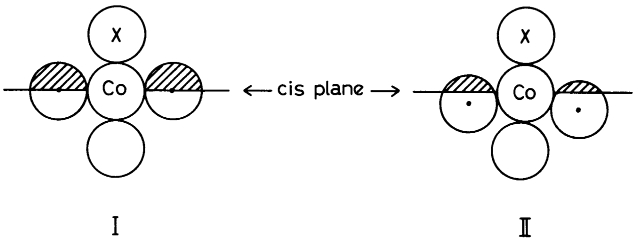

Fig. 5. Schematic expression of V_{do} (shaded part) of thiocyanato or isothiocyanato complex ($[CoXA_5]$). X denotes sulfur or nitrogen atom in thiocyanate. When $[CoXA_5]$ is a regular octahedron in geometry, V_{do} corresponds to V_{ro}. I: Regular octahedral $[CoXA_5]$. II: Distorted octahedral $[CoXA_5]$.

TABLE 8. THE V_{do} AND R_v VALUES OF THE THIOCYANATO AND ISOTHIOCYANATO COMPLEXES AND RELATED COMPLEXES

Complex	Co–X bond	V_{do}/Å^3	R_v	Ref
$[Co(NCS)(hedtra)]^-$	Co–N(NCS)	1.84	0.73	This work
$[Co(SCN)(edtra)]^-$	Co–S	2.14	0.85	This work
$[Co(Hedta)(H_2O)]$	Co–O(H_2O)	2.22	0.88	8
$[Co(NO_2)(edtra)]^-$	Co–N(NO_2)	2.12	0.84	9
$[Co(SCN)(NH_3)_5]^{2+}$	Co–S	2.91	1.01	15
$[Co(NH_3)_5(NCS)$- in dimer[a]	Co–N(NCS)	3.00	1.04	12
$[Co(CN)_5(SCN)$- in dimer[a]	Co–S	3.83	1.00	12

a) Dimer means $[(NH_3)_5Co(NCS)Co(CN)_5]$.

$$\sum_{cis} V_{ro} = \frac{1}{2}(\text{the sum of the volume occupied by the donor atoms } A_1, A_2, A_3, \text{ and } A_4) \qquad (2)$$

Therefore, if the complex in question takes the geometry of a regular octahedron, the R_v value must be unity. When there is a large open space around the coordination site of the thiocyanato ligand, the R_v value becomes smaller than unity. In the calculation of the R_v values, all donor atoms are assumed to be spherical and have covalent radii (C, 0.77; N, 0.70; O, 0.66).[20] The R_v and V_{do} values thus obtained are summarized in Table 8. For the $[Co(NO_2)(edtra)]^-$ and $[Co(Hedta)(H_2O)]$ complexes, the Co–NO_2 and Co–OH_2 bonds are regarded as Co–SCN (or NCS) bond.

There is a remarkable difference between the R_v values of the complexes containing diamine-*N,N'*-polycarboxylate and the other complexes: The former complexes show smaller R_v values (<0.9) than the latter complexes (≈1). This means that the pentaammine and pentacyano complexes are almost regular octahedral in geometry, while the complexes containing diamine-*N,N'*-polycarboxylates are considerably distorted octahedral molecules so that very open spaces are created around the Co–X bond (X=SCN^-, NCS^-, H_2O, or NO_2^-). Therefore, the sixth coordination sites of the pentaammine and pentacyano complexes which accommodate thiocyanato ligand are more crowded than those of the diamine-*N,N'*-polycarboxylato complexes.

Steric Factor Controlling the Formation of the Thiocyanato and Isothiocyanato Linkage Isomers. The reactions of $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(CN)_5(H_2O)]^{2-}$ with SCN^- lead to the almost exclusive formation of N-bonded isomers.[1,2] In the system of $[CoL(H_2O)]^{n-}$ containing diamine-*N,N'*-polycarboxylate ion, however, spontaneous formation of both N-bonded and S-bonded isomers was observed. This may be due to the difference in the steric circumstances around the coordination sites which accommodate thiocyanate ions.

The substitution reactions of $[Co(NH_3)_5(H_2O)]^{3+}$, $[Co(CN)_5(H_2O)]^{2-}$, and $[CoL(H_2O)]^{n-}$ will proceed through D or I_d mechanism to produce five coordinate intermediate, because substitution reactions of most cobalt(III) complexes have been believed to proceed through the mechanism.[21] The vacant coordination site of the intermediate yielded from $[CoL(H_2O)]^{n-}$ would be much less crowded than those from $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(CN)_5(H_2O)]^{2-}$.

The size of a sulfur atom is larger than that of a nitrogen atom. The Co–SCN bond in S-bonded isomers is bent (<CoSC=≈100°), while the Co–NCS bond is approximately linear. Therefore, the coordination of the sulfur end in thiocyanate ion requires a larger open space around the coordination site than that of the nitrogen end. The smaller open space in $[Co(NH_3)_5]^{3+}$ and $[Co(CN)_5]^{2-}$ intermediates cannot accept the sulfur end favorably, but the larger open space in $[CoL]^{n-}$ intermediate can accept not only the nitrogen end but also the bulky sulfur end.

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