

The Crystal Structures and Isomerization of the Linkage Isomers Thiocyanato- and Isothiocyanatopenta-amminecobalt(III) Dichloride, $[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$

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The thiocyanato isomer $[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ crystallizes in space group $P2_12_12_1$ with cell parameters $a = 8.74$ (1), $b = 8.74$ (1) and $c = 14.52$ (2) Å. The isothiocyanato isomer $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$ is disordered in space group $Fm\bar{3}m$ with $a = 10.16$ (2) Å. In the former structure the CoSCN moiety is bent, the angle at sulphur being 105 (1.1)°. No structural *trans* effect of the thiocyanate group was found. All Co-N are equivalent within error and average 1.94 Å. The Co-S bond length is 2.272 (7) Å. The thiocyanate isomer slowly transforms to the isothiocyanate under X-irradiation with the following orientation transformation of their cell vectors: $O[001]$ becomes $C[110]$, $O[010]$ becomes $C[001]$ where O and C denote the orthorhombic and cubic cells. The transformed structure gives a very similar diffraction pattern to that of the isothiocyanate complex crystallized from water. This structure is disordered such that a cobalt atom at (0,0,0) has $\frac{5}{6}$ of an NH_3 group and $\frac{1}{6}$ of a NCS group coordinated to it along $[100]$. The octahedral complex ion has the expected linear isothiocyanate coordination, but the overall accuracy of the bond lengths is low because of the disorder. Integrated precession film data and visually estimated in addition to integrated Weissenberg film data were used for the structure analyses. Both structures have been refined by full-matrix least-squares methods giving $R_1 = 0.097$ for the thiocyanate and 0.077 for the isothiocyanate where R_1 is based on F , and 1109 unique reflexions were used in the former refinement and 47 in the latter.

Introduction

The structure analysis of the thiocyanate complex was undertaken to structurally characterize thiocyanate bonding to cobalt(III) and to determine whether thiocyanate produces a structural *trans* effect with this metal. A similar lengthening of a bond *trans* to thiocyanate has been detected in a palladium complex (Clark & Palenik, 1970). Buckingham, Creaser & Sargeson (1970) have shown that the thiocyanate isomer isomerizes in the solid and in solution under mild conditions. In solution this reaction proceeds by an intramolecular mechanism and it was of interest to see if the solid state mechanism could be deduced by X-ray structure analysis of both isomers.

Experimental

Crystals of both isomers were kindly supplied by Dr D. A. Buckingham and prepared by us (Buckingham *et al.*, 1970). The cell constants were determined from precession photographs with $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107$ Å). Crystal data are given in Table 1.

Isomerization

Crystals of the thiocyanate isomer (S-bonded) grow as needles elongated along $[001]$ and display the faces (110) and (011). They isomerize under X-irradiation (80 to 100 hr with $\text{Mo } K\alpha$ radiation from a tube operated at 50 kV, 20 mA) and the initial set of sharp reflexions is replaced by a diffuse set which corresponds

Table 1. *Crystal data*

E.s.d.'s are given here and elsewhere in parentheses.		
	$[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	$[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$
F. W.	291.1	273.1
Space group	$P2_12_12_1$	$Fm\bar{3}m$
a	8.74 (1) Å	10.16 (2) Å
b	8.74 (1)	—
c	14.52 (2)	—
D_m	1.74 (2) g.cm^{-3}	1.76 (2) g.cm^{-3}
D_c	1.743	1.729
U	1109 (3) Å ³	1049 (3) Å ³
Z	4	4
$\mu(\text{Mo } K\alpha)$	14.35 cm^{-1}	15.06 cm^{-1}
$F(000)$	600	560

to the isothiocyanate isomer (N-bonded) lattice. The initially pink crystal changes colour to orange, characteristic of the isothiocyanate isomer, but remains unfractured and clear. Isomerization also occurs (Buckingham *et al.*, 1970) in infrared radiation (1 hr in a spectrophotometer) and thermally (1 day at 80°C).

The remarkable solid state features of the isomerization are the close relationship of the lattices of substrate and product, the coherence of the product crystal and the relatively small degree of mosaic block disorder apparent in the product photograph. Fig. 1 shows the unit cell relationships. The orthorhombic lattice of $[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ appeared to change to the body-centred tetragonal lattice ($7.20 \times 7.20 \times 10.16$ Å) shown as broken lines in Fig. 1. In this

transformation the orthorhombic *c* repeat distance is halved and the tetragonal cell edges are parallel to those of the initial orthorhombic cell. It was later realized that the product lattice was face-centred cubic with axes as shown in Fig. 1. This was confirmed using the polarizing microscope and by data reduction of the intensities in Laue group *m3m*.

Zero-layer Weissenberg photographs taken with the *c* axis of the orthorhombic cell as rotation axis show the product intensities streaked parallel to this axis. Each reflexion records over 20° of rotation and consists of broad maxima centred at 3, 10 and 17° from one end with peak intensities in the ratio 1:2.5:1. This distribution was evident in several product crystals and must correspond to a symmetrical and non-gaussian distribution of mosaic-block orientation in the crystal. The central region is broader and has an integrated intensity of roughly fifteen times that of the sharper end peaks. This may account for the observation that on precession photographs (*0kl*, *h0l*) the product reflexions lie on 10° arcs and do not show multiple maxima.

Data collection - [Co(SCN)(NH₃)₅]Cl₂.H₂O

Integrated precession and visual Weissenberg data were collected with zirconium-filtered Mo *K*α radiation with five crystals as follows:

Table with 3 columns: Crystal, Camera, Levels. It lists 5 different crystal specimens and their corresponding camera setups and level ranges.

Five crystals were used to avoid isomerization; crystals 3 to 5 were cut from the same single crystal. In all cases the needle axis (*c*) was the rotation axis. The Weissenberg levels were simultaneously recorded in adjacent pairs with μ set at the average value of the equi-inclination angles. The setting-angle error introduced (approximately 40') was small but was sufficient to minimize possible multiple-reflexion effects (Yakel & Fankuchen, 1962). Film packs (three films each) incorporating brass sheet (0.0025 cm) and giving film factors of 3.1 to 3.5, were used. The integrated precession data were measured with a non-scanning microdensitometer. The data were corrected for Lorentz and polarization effects, but not for absorption. The extended upper level Weissenberg data were all corrected for spot extension using the same polynomial,

(L+ΔL)/L = 2.89 - 0.22 * ψ/2 + 6.38 × 10^-3 * (ψ/2)^2

obtained by least-squares fit to the measured spot lengths. Interfilm and interlayer scale factors were determined by the non-iterative least-squares algorithm of Rae (1965) using procedures described previously (Snow, 1970). From 1532 measured reflexions,

Table 2. Observed and calculated structure factors for [Co(SCN)(NH₃)₅]Cl₂.H₂O (upper sets) and for [Co(NCS)(NH₃)₅]Cl₂ (last set) in electrons × 10⁻⁴

Large multi-page table containing observed and calculated structure factors for various hkl indices. It is organized into several sections and includes columns for h, k, l, F_o, and F_c.

Final section of Table 2 containing the last set of structure factor data for [Co(NCS)(NH₃)₅]Cl₂.

1109 unique reflexions representing 84% of those accessible within a Cu K α limiting sphere were obtained on scaling, 280 of which were unobserved.

Data collection – [Co(NCS)(NH₃)₅]Cl₂

The crystals of the isothiocyanate isomer grow as well formed octahedra. Integrated Weissenberg and precession data were collected with a crystal of size 0.3 × 0.25 × 0.25 mm. With respect to the body-centred tetragonal cell (dotted, Fig. 1) the levels collected were: equi-inclination Weissenberg, *h0l* to *h5l*; precession, *hk0* to *hk2*. Three films per pack and three separate exposures per level were used. The reflexions were measured by densitometry and processed as for the thiocyanate isomer though spot extension corrections were not made because only the compacted Weissenberg reflexions were estimated. The tetragonal indices (*hkl*) were transformed to cubic (*h'k'l'*) using the relationships: *h'* = *h* + *k*, *k'* = *h* - *k*, *l'* = *l*, and the unique reflexions were extracted during interlevel scaling assuming Laue symmetry *m3m*. The symmetry was confirmed by the good internal agreement of the reflexions averaged in this Laue symmetry. Only 47 unique reflexions above background were obtained, corresponding to 5.8% of the unique lattice points within the Cu K α limiting sphere. The low total is primarily due to the rapid fall-off in intensity with angle from this centric structure.

Structure determination and refinement

[Co(NH₃)₅SCN]Cl₂ · H₂O

The structure was solved from the Patterson synthesis. Two atoms had to be found to initiate the heavy-atom phasing process since the *x* coordinate of the Co atom was very close to 0.25 and consequently this atom could not contribute to all the reflexions. Once the Co and S atoms had been correctly sited the remaining atoms excepting those of the water molecule could be readily sited from successive Fourier maps. These atoms were refined by full-matrix least-squares

methods using isotropic temperature factors to $R_1 = 0.15$ ($R_1 = \sum |F_o| - |F_c| / \sum |F_o|$). A difference synthesis at this stage revealed the water molecule and showed evidence of anisotropy in many of the other atoms. Refinement converged with $R_1 = 0.101$, all atoms except the oxygen of the water molecule having anisotropic temperature factors. Analysis of the quantity minimized in the refinement [$\sum w(F_o - F_c)^2$ versus F_o] showed that it increased rapidly with F_o . The weights that had been assigned during data reductions (Snow, 1970) were unsatisfactory as confirmed by an irregular molecular geometry of the complex and a negative definite thermal ellipsoid for the oxygen atom of the water molecule obtained on attempting to refine the atom anisotropically. Refinement was resumed with a Hughes weighting scheme, $\sigma = 5.5$ for $F_o < 40$, $\sigma = 0.138 F_o$ for $F_o > 40$. Three cycles of refinement gave $R_1 = 0.097$ (excluding reflexions below background which were not refined) and $R_2 = 0.132$ ($R_2 = [\sum w(F_o - F_c)^2] / \sum w F_o^2$).

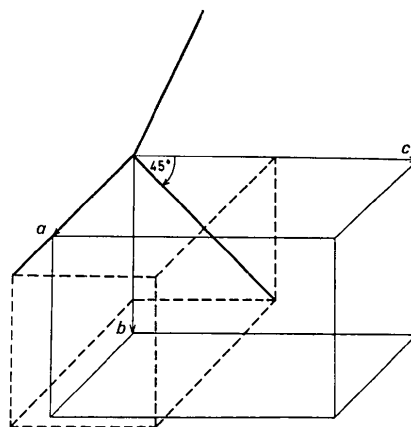


Fig. 1. Relationship between the orthorhombic unit cell of [Co(SCN)(NH₃)₅]Cl₂ · H₂O (bold cell, *a*, *b*, *c* shown), the cell edges of cubic [Co(NCS)(NH₃)₅]Cl₂ (very bold), and the tetragonal cell of the latter crystal used for data collection.

Table 3. Final positional and thermal parameters for [Co(SCN)(NH₃)₅]Cl₂ · H₂O

The anisotropic temperature factor has the form:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \cdot$$

All parameters are multiplied by 10⁴.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2366 (4)	435 (3)	1293 (2)	71 (4)	61 (3)	15 (1)	-5 (4)	-1 (2)	1 (2)
S	1316 (7)	2813 (7)	1284 (5)	83 (8)	103 (8)	38 (3)	-10 (8)	8 (5)	4 (5)
Cl(1)	743 (9)	1854 (7)	4066 (4)	149 (11)	88 (7)	32 (2)	17 (9)	-4 (5)	8 (4)
Cl(2)	2792 (9)	-2606 (9)	3523 (4)	165 (12)	167 (10)	28 (2)	31 (11)	-1 (5)	10 (4)
N(1)	3126 (27)	-1640 (21)	1336 (14)	196 (41)	69 (22)	29 (8)	39 (27)	11 (20)	32 (13)
N(2)	1177 (29)	-103 (22)	209 (11)	188 (43)	89 (26)	16 (6)	-78 (32)	-16 (16)	4 (11)
N(3)	660 (23)	-128 (24)	2100 (13)	83 (27)	115 (29)	32 (9)	-16 (29)	10 (14)	7 (14)
N(4)	4010 (23)	1074 (21)	491 (12)	96 (29)	74 (23)	28 (8)	-51 (28)	17 (14)	15 (12)
N(5)	3597 (22)	923 (24)	2373 (11)	74 (24)	145 (31)	13 (6)	35 (28)	-1 (11)	-5 (12)
C	2777 (37)	3985 (29)	1220 (19)	149 (48)	117 (33)	43 (13)	51 (45)	14 (27)	27 (19)
N(6)	3725 (29)	4874 (28)	1208 (23)	136 (39)	128 (36)	109 (22)	-35 (36)	82 (27)	9 (26)
O	3496 (24)	3919 (23)	3643 (19)	185 (38)	147 (32)	90 (17)	-129 (33)	5 (24)	3 (21)

[Co(NH₃)₅NCS]Cl₂

The cubic space group *Fm3m* requires the complex cation to be disordered. The Patterson synthesis confirmed the allocation of sites as in Table 4. The ammine and thiocyanate nitrogen atoms are indistinguishable in the model and were refined together. The full-matrix least-squares refinement converged after four cycles, with $R_1=0.077$, $R_2=0.065$. Correlation coefficients greater than 0.5 were found between the parameters as follows: all thermal parameters except that of carbon in one group, and between the sulphur positional and thermal parameters and the carbon position in a second group. The weighting scheme used was that derived during data reduction. Analysis of $\sum w(F_o - F_c)^2$ versus F_o showed no systematic trend, but fluctuated widely. The latter effect is most probably due to the small number of reflexions in each F_o range. A final difference synthesis showed a diffuse positive region around the Co atom (peak, 0.3 e.Å⁻³). The positive region about cobalt extended just beyond the nitrogen sites to regions where disordered hydrogen atom sites would be expected. The density was diffuse however and no definite ring of density due to these was present.

For Co and Cl the atomic scattering factors of Doyle & Turner (1968; Co²⁺ and Cl⁻) were used and for S, O, N and C, the neutral curves of Ibers (1962). Only real dispersion corrections were applied for Co, Cl and S ($f' = +0.3$, $+0.1$ and $+0.1$ respectively). The CDC 6400 computer programs used were those described previously (Snow, 1970). The observed and calculated structure factors for both isomers are given in Table 2. Table 3 contains the positional and thermal parameters of the thiocyanate crystal, Table 4 contains the same data for the isothiocyanate isomer.

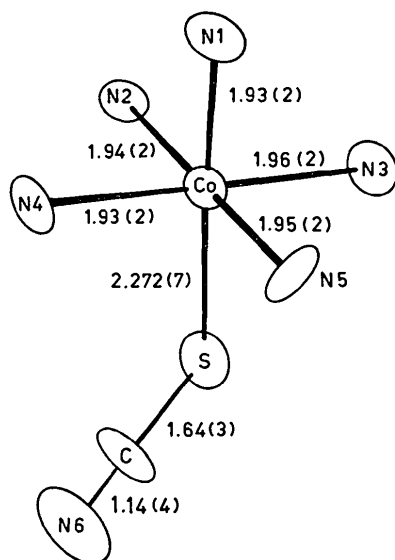


Fig. 2. Bond lengths and atom numbering of the [Co(SCN)(NH₃)₅]²⁺ cation.

Table 4. Least-squares parameters for [CoNCS(NH₃)₅]Cl₂

	Occupancy	x	y	z	B
Co	1.0000	0.0	0.0	0.0	5.0 (0.2) Å ²
Cl	1.0000	0.25	0.25	0.25	11.2 (0.3)
S	0.1666	0.460 (6)	0.0	0.0	4.8 (1.8)
N	1.0000	0.191 (2)	0.0	0.0	9.9 (0.5)
C	0.1666	0.336 (11)	0.0	0.0	4.5 (2.3)

Results and discussion

Thiocyanate isomer

The atomic numbering and bond lengths are given in Fig. 2. The bond angles appear in Table 5. It is evident from Fig. 2 that no structural *trans* effect is present at this level of precision, the Co-N(1) bond [1.93 (2) Å] is very close to the mean Co-N bond length [1.944 (5) Å, error in the mean estimated by internal agreement of the Co-N bonds]. This mean value is shorter than values reported for Co(III) hexa-ammine and penta-ammine complexes [Co(NH₃)₆]I₃ by Barnet, Craven, Freeman, Kime & Ibers (1962), 1.96 Å; [Co(NH₃)₅Cl]Cl₂ by Messmer & Amma (1968, 1.97 Å). This shortening of approximately 0.02 Å is significant on comparison of the mean bond lengths and may be due to differences in thermal motion of the ammine groups between these structures. Corrections for thermal motion have not been applied in any of these structures and the accuracy of the thiocyanate structure would not appear to justify them since hydrogen atoms have not been inserted into the model and no absorption corrections have been made. The root mean square displacements of the atoms along the principal axes of the thermal ellipsoids show that for the ammine nitrogen atoms the displacements along the bonds (0.08 to 0.13 Å) are much less than those orthogonal to them (0.16 to 0.26 Å). The Co-S distance of 2.272 (7) Å is very close to that [2.284 (6) Å] found in the thio-sulphate cation [Co(NH₃)₅S₂O₃]⁺ by Baggio (1970), where the Co-S-S angle is 110.5° and the bonding situation appears to closely approach that in the thiocyanate complex. The bond length is also very close to the sum of the covalent radii (2.26 Å) taking 1.22 Å (Barnet *et al.*, 1966) for cobalt(III) and 1.04 Å for tetrahedral sulphur (Pauling, 1960). The bond angle at sulphur (104.9°) lies closer to the values recently found in palladium compounds [e.g. K₂Pd(SCN)₄ by Mawbry & Pringle (1970), 101 and 109°; Pd[(C₆H₅)₂PCH₂-CH₂-CH₂N(CH₃)₂]₂(SCN)-(NCS), by Clark & Palenik (1970), 107.3°] than to the value of 90° reported for a five-coordinate copper complex (Marongiu, Lingafelter & Paoletti, 1969). In this latter square pyramidal triethylenetetramine complex the Cu-S bond is quite long (2.6 Å) and close intramolecular contacts with the thiocyanate group are not made. In the cobalt complex the carbon atom has contacts with N(4), 2.96 Å and N(5), 3.24 Å which are respectively less than and close to the sum of non-bonded crystal contact radii

(3.25 Å) tabulated by Bondi (1964). It is evident that the M-S-C angle cannot approach 90° in the cobalt complex because of these repulsive non-bonded interactions. The S-C and C-N bond lengths lie well within the range of the above complexes.

Table 5. Bond angles
in the [CoSCN(NH₃)₅]²⁺ cation

Angle		Angle	
Co—S—C	104.9 (1.1)°	N(1)—Co—N(4)	92.0 (8)°
S—C—N	175.0 (3.0)	N(1)—Co—N(5)	89.4 (8)
S—Co—N(1)	176.0 (6)	N(2)—Co—N(3)	91.0 (8)
S—Co—N(2)	90.1 (6)	N(2)—Co—N(4)	88.8 (8)
S—Co—N(3)	85.7 (6)	N(2)—Co—N(5)	178.3 (8)
S—Co—N(4)	91.9 (6)	N(3)—Co—N(4)	177.6 (8)
S—Co—N(5)	91.6 (6)	N(3)—Co—N(5)	89.6 (8)
N(1)—Co—N(2)	89.0 (8)	N(4)—Co—N(5)	90.7 (8)
N(1)—Co—N(3)	90.4 (8)		

The cations are held together by an extensive series of hydrogen bonds in which all atoms other than cobalt and carbon appear to be involved. The structure is

Table 6. Intermolecular contacts (≤ 3.6 Å)
in the [CoSCN(NH₃)₅]Cl₂ · H₂O crystal

Possible hydrogen bonds are indicated by H.

Distance (Å)		Distance (Å)	
Cl(1)—N(3 ⁱ)	3.34 H	O—N(5 ⁱ)	3.20
Cl(1)—N(5 ⁱ)	3.60	O—C(1 ⁱ)	3.58
Cl(1)—O(1 ⁱ)	3.07 H	O—Cl(1 ⁱ)	3.07 H
Cl(1)—N(1 ⁱⁱ)	3.45	O—Cl(2 ^{vi})	3.10 H
Cl(1)—N(2 ⁱⁱ)	3.51	O—N(1 ^{vii})	2.99 H
Cl(1)—N(4 ⁱⁱ)	3.30 H	O—N(4 ^{vii})	3.14
Cl(1)—N(2 ^{iv})	3.32 H	O—N(5 ^{vii})	3.42
Cl(1)—N(3 ^{iv})	3.37		
		S—N(3 ^{iv})	3.42 H
Cl(2)—N(1 ⁱ)	3.30 H	S—N(4 ^{viii})	3.41 H
Cl(2)—N(3 ⁱ)	3.53	N(6)—N(2 ⁱⁱⁱ)	2.98 H
Cl(2)—N(5 ⁱ)	3.58	N(6)—N(1 ^{vi})	3.10 H
Cl(2)—N(2 ⁱⁱ)	3.52	N(6)—N(5 ^{vii})	3.25
Cl(2)—N(4 ⁱⁱ)	3.53		
Cl(2)—N(4 ^v)	3.35 H		
Cl(2)—O(1 ⁱ)	3.10 H		

Code for asymmetric units

I	x, y, z	V	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
II	$x-\frac{1}{2}, -y, \frac{1}{2}+z$	VI	$x, -1+y, z$
III	$x+\frac{1}{2}, \frac{1}{2}-y, -z$	VII	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	VIII	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$

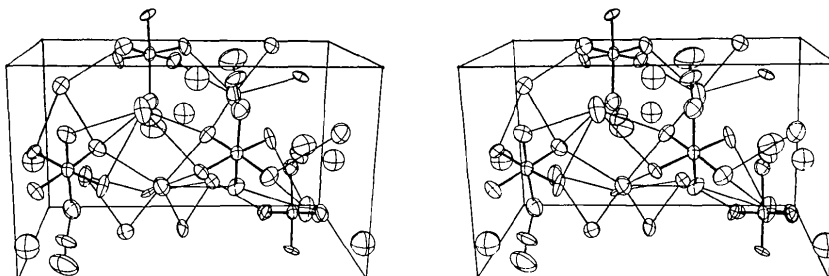


Fig. 3. Stereoscopic diagram of the unit cell of [Co(SCN)(NH₃)₅]Cl₂ · H₂O. The origin is at the rear lower right with axes $\searrow a$, $\uparrow b$ and $\leftarrow c$. Close contacts with chloride are shown.

shown in Fig. 3, and Table 6 lists intermolecular contacts and possible hydrogen bonds. The ammine nitrogen atoms have the following numbers of close contacts: N(1), 4; N(2), 4; N(3), 4; N(4), 5 and N(5), 5. All these contacts cannot be hydrogen bonds; the contacts indicated by H in Table 5 are within ± 0.1 Å of the hydrogen bond distances tabulated by Hamilton & Ibers (1968). On this basis the numbers of hydrogen bonds to each ammine nitrogen are: N(1), 3; N(2), 2; N(3), 2; N(4), 3 and N(5), 0.

Isothiocyanate isomer

The bond lengths are summarized in Fig. 4, representing a cell edge of the cubic crystal.

Because the structure is disordered and the carbon site averages only one electron, the bond lengths to carbon are especially ill defined. However, the N to S distance [2.73 (6) Å], is close to the value determined for the thiocyanate isomer [2.77 (3) Å].

Each chloride site is surrounded in tetrahedral array by cobalt octahedra (Co and 6N atoms) and each cobalt octahedron is surrounded by eight chloride ions. The Cl...N distance is 3.55 (2) Å and is probably a weak hydrogen bond. These interactions and the S...N' contact shown above which is close to the sum of the van der Waals radii (3.4 Å) are the main intermolecular contacts. The temperature factor of the chloride ion (11.2 Å²) is unusually high and it is probable that this reflects disorder about the $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ type sites to accommodate the disordered cation. It is noteworthy that the compound [Co(NCS)(NH₃)₅](NO₃)₂ also crystallizes in space group *Fm3m* (Gowda, Banerjee & Fletcher, 1970) although no structural details have been reported. Crystals of [RuN₂(NH₃)₅]X₂ also have similar disordered structures (space group *Fm3m* X = Cl⁻, $a = 10.19$; X = Br⁻, $a = 10.41$; X = I⁻, $a = 10.94$ Å, Bottomley & Nyburg, 1966). This fluorite type structure is not preferred by all [M(X)(NH₃)₅]Y₂ crystals. Thus [Co(CN)(NH₃)₅]Cl₂ and [Ru(CO)(NH₃)₅]Cl₂ (Stanko & Starinshak, 1969) adopt an orthorhombically distorted version of it. The complex [CoCl(NH₃)₅]Cl₂ does not adopt it (Messmer & Amma, 1967), but the recently prepared complex [Ru(NNO)(NH₃)₅]Br₂ (Diamantis & Sparrow, 1971) does. No ready rationalization of these facts can be offered.

Isomerization mechanism

Close comparison of the diffraction intensities of the isothiocyanate isomer crystallized from water with the thiocyanate decomposition product show good visual agreement. The former crystal is anhydrous (D_c for $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$ is 1.73, D_c for a monohydrate is 1.84, $D_m = 1.76 \text{ g.cm}^{-3}$). The decomposition product must accommodate a disordered water molecule.* Spectrophotometric analysis of the product (Buckingham, 1971) shows that little, if any $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ complex ion is formed. The displacements of the four cobalt centres during isomerization average 1.75 Å. With respect to an origin on a cobalt in the thiocyanate complex the remaining cobalt centres must move 3.3, 1.9 and 1.8 Å to achieve the cubic isothiocyanate structure. Two basic mechanisms are conceivable to account for the cubic disordered product. In the first, rupture of a Co-S bond leads to a subsequent random acceptance by the $[\text{Co}(\text{NH}_3)_5]^{3+}$ intermediate of the nitrogen end of a thiocyanate ion from any direction followed by minor reorganisation to achieve the product structure. The second mechanism requires Co-S bond rupture and subsequent recapture of the N end of thiocyanate by the same cobalt. Reorganisation of the $[\text{Co}(\text{NCS})(\text{NH}_3)_5]^{2+}$ ions to achieve the disordered cubic structure would then have to follow. We believe the former process would be more readily achieved with minimum disruption of the crystal. The large rotations of the elongated complex ions (N-Co-NCS has an effective length 3 Å longer than N-Co-N) required by the latter process would probably lead to fragmentation of the crystal. The operation of the former (intermolecular) mechanism could also be expected to produce quantities of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, which were not found. Differing electronic reorganisation energies of bond formation to Cl^- and NCS^- together with the involvement of Cl^- in many hydrogen bonds may account for non-formation of the chloropenta-ammine. Radioisotope tracer

* We are grateful to the referees for pointing out that the isomerization product need not have a density approaching 1.84 g.cm^{-3} . Its cell could not be accurately measured and need not be identical to that found for the material crystallized from water.

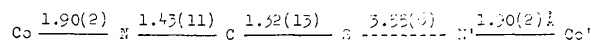


Fig. 4. Cell edge of the cubic crystal of the isothiocyanate isomer

experiments are planned to resolve this question of mechanism.

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