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CRYSTAL STRUCTURES OF COBALT(III) AMMINES WITH AN INNER-SPHERE THIOCYANATO GROUP

$[Co(NH_3)_5NCS]X_2$ ($X = NO_3$, Cl, NCS)

In complex compounds the thiocyanato group can form coordination bonds of three types

I. M—NCS. II. M—SCN. III. M—SCN—M.

Here M is the metal complex-forming atom. The type of coordination depends on the nature of the central atom and of the ligand partners.

The aim of the present work was to determine the coordination and configuration of the NCS group in Co(III) ammines. The results of a preliminary structural investigation of $[Co(NH_3)_5NCS](NO_3)_2$ have already been reported by us ([1]). From Patterson syntheses it was established that the bond of the thiocyanato group to Co in this pentamminorhodanide is effected through the N atom; five NH_3 groups and one NCS group are distributed statistically over the vertices of an octahedron around Co.

A more detailed investigation of the structure of thiocyanatopentamminecobalt nitrate with final refinement was carried out by Fourier-synthesis methods. Of the three possible Fedorov groups $O_h^5 = Fm3m$, $O^3 = F432$, and $T_d^2 = F43m$, the noncentrosymmetric ones were excluded on the basis of goniometric data and the negative result of rotating the plane of polarization. Calculation of the structure amplitudes $F_T(hkl)$ for the centrosymmetric case, taking into account the coordinates of Co, N (inner-sphere), and S atoms, changed the signs of only two reflections, (333) and (828), out of an array of 76 independent reflections. The signs obtained were taken into account in constructing a linear section of the electron density along the space diagonal ([2]). On one quarter of the diagonal (Fig. 1) a distinct maximum of electron density is distinguished, which was identified with the N atom of the NO_3 group from the second coordination sphere. The NO_3 complex as a whole occupies eightfold positions at the centers of the eight octants of the cell.

Fig. 1. Electron-density distribution curve along the space diagonal of the unit cell of the crystal $[Co(NH_3)_5NCS](NO_3)_2$

Figure 1: Fig. 1. Electron-density distribution curve along the space diagonal of the unit cell of the crystal $[Co(NH_3)_5NCS](NO_3)_2$

Fig. 2

Figure 2: Fig. 2

Fig. 1. Electron-density distribution curve along the space diagonal of the unit cell of the crystal
$[Co(NH_3)_5NCS](NO_3)_2$

The contribution of the O atoms of the NO_3 group to the structure amplitudes was calculated for two variants: in one, the O atoms rotated around N; in the other, their statistical distribution was assumed.

Allowance for free rotation of the O atoms around N in a plane perpendicular to the body diagonal was carried out according to ([3,4]). For atoms remaining in their plane,

$$F = \sum_{j=1}^{N} f_j J_0(x_j),$$

where $J_0(x_j)$ is the Bessel function of zero order with argument

$$x_j = 4\pi a_j \frac{\sin\vartheta}{\lambda} \sin\alpha;$$

a_j is the distance of the O atoms from the axis of rotation, taken as equal to 1.2 Å, i.e., the N–O bond length in the nitrate ion; α is the angle between the plane containing the rotating atoms and the reflecting plane. The discrepancy factor calculated with allowance for rotation of the atoms is 19.2% ($B = 2.5$ Å^2).

For the variant with a statistical distribution of O atoms over 96-fold positions (on the symmetry plane m) in the Fedorov group $O_h^5 = Fm3m$, the coordinates x and z were calculated from the available standard interatomic distances N–O in the nitrate ion. The structural amplitudes $F(hkl)$, after introduction of the coordinates of the O atoms, led to a factor $R = 16.5\%$ ($B = 2.5$ Å^2). The 15% decrease (relative) of the discrepancy factor for the second variant indicated that in the structure of thiocyanatopentaamminecobalt nitrate the statistical distribution of 24 O atoms over 96-fold positions is more probable than rotation of the angular nitrate group.

Fig. 2. Projection of the electron density on the plane (001), in el/Å^2. Contour lines are drawn at intervals of 2 el/Å^2. The dashed line corresponds to 2 el/Å^2.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Weighted projection of the electron density $C_1(xy)$. Contour lines are drawn at intervals of 2 el/Å^2; regions of negative values are indicated by dashed lines.

Refinement of the coordinates of the N and S atoms for the structural variant with a statistical distribution of O atoms in the NO_3 group was carried out from the weighted projection and the linear section of the electron density along the edge of the unit cube. Figs. 2 and 3 show the final projections of the electron density $\sigma(xy)$ and $C_1(xy)$.

The atomic coordinates found from the weighted and linear Fourier syntheses were averaged and are given in Table 1 (the x coordinate of the C atom, occupying 24-fold positions on the coordinate axes with probability 1/6, was calculated on the basis of standard data on the N–C bond length in the linear isothiocyanato group).

The final discrepancy factor of the structure for experimental reflections different from zero is 14.2% ($\sin\vartheta/\lambda \leq 0.75$ Å^{-1}, $B = 2.6$ Å^2).

The interatomic distances in the structure $[Co(NH_3)_5NCS](NO_3)_2$, calculated from the corresponding R coordinates, have the following values ($a = 10.687 \pm 0.08$ Å):

$$Co - N(NH_3) = Co - N(NCS) = 1.95 \text{ Å}; \qquad N - C = 1.14 \text{ Å};$$

$$C - S = 1.56 \text{ Å}; \qquad Co - N(NO_3) = 4.63 \text{ Å}; \qquad N - O = 1.24 \text{ Å}.$$

Figure 4 gives a projection of 1/4 of the unit cell of $[Co(NH_3)_5NCS](NO_3)_2$ onto the xy plane.

The X-ray structural study of thiocyanatopentaamminecobalt chloride $[Co(NH_3)_5NCS]Cl_2$ was carried out by the powder method from Debye patterns (RKU-86 camera) with an asymmetric film loading, using CoK_α- and FeK_α-

Table 1

Coordinates of the basis atoms of the structure of thiocyanatopentaamminecobalt nitrate
$[Co(NH_3)_5NCS](NO_3)_2$

Fig. 4. Projection of 1/4 of the cell of $[Co(NH_3)_5NCS](NO_3)_2$ onto the xy plane

Figure 4: Fig. 4. Projection of 1/4 of the cell of $[Co(NH_3)_5NCS](NO_3)_2$ onto the xy plane

Atoms and their number in the cell	Multiplicity, position, and point symmetry	x	y	z
4Co	$4(a)$, $m3m$	0	0	0
$20N(NH_3)$ and 4N(NCS)	$24(e)$, $4\,mm$	0.1826	0	0
4C(NCS)	$24(e)$, $4\,mm$	0.289	0	0
4S(NCS)	$24(e)$, $4\,mm$	0.435	0	0
$8N(NO_3)$	$8(c)$, $\bar{4}3m$	0.250	0.250	0.250
$24O(NO_3)$	$96(k)$, m	0.202	0.202	0.345

radiations (single crystals suitable for X-ray goniometric studies could not be obtained). The X-ray diagrams were measured on an MF-4 microphotometer with a reading accuracy of $\sim$ 0.1 mm. The indexing results establish that the crystals belong to the cubic system with an F-cell, $a = 10.23 \pm 0.02$ Å. The crystal density was determined (pycnometrically in toluene) as $\rho_{expt} = 1.72$ g/cm^3. With four formula units of $[Co(NH_3)_5NCS]Cl_2$ in the elementary cube, the corresponding X-ray density is $\rho_{calc} = 1.69$ g/cm^3.

Intensities were determined quantitatively by photometry of the blackening on the Debye patterns. To obtain relative intensity values, the procedure of ([5]) was used. From the obtained $|F|^2$ values (without taking the absorption factor into account), linear vector diagrams $P(x00)$ and $P(xxx)$ were constructed.

In the direction of the cube edge, a peak was found at a distance of 1.95 Å from the Co atom, which corresponds to the sum of the covalent radii and to the vector Co—N in $[Co(NH_3)_5NCS]\cdot(NO_3)_2$, with octahedral coordination around Co by five NH_3 groups and a sixth N from the NCS group.

Fig. 4. Projection of 1/4 of the cell of $[Co(NH_3)_5NCS](NO_3)_2$ onto the xy plane

From the linear vector diagram along the direction of the threefold axis, it followed clearly that the chlorine atoms of the outer sphere are located at the centers of the octants of the cell, i.e., the distance Co—Cl is $A\sqrt{3}/4 = 4.43$ Å. A graphical comparison of the calculated (the coordinates of the C and S atoms were obtained from the interatomic distances N—C and C—S in the

linear isothiocyanato group) and experimental structural amplitudes showed their satisfactory agreement.

Crystals of $[Co(NH_3)_5NCS](NCS)_2$ are octahedra of carmine-red color. The Laue symmetry is $O_h = m3m$. The lattice parameter, calculated initially from an oscillation photograph, was refined from a powder photograph with a NaCl standard: $a = 10.94 \pm 0.03$ Å. At a sample density of $\rho_{expt} = 1.63$ g/cm^3, the elementary cube contains 4 units of the indicated composition ($\rho_{calc} = 1.61$ g/cm^3).

In a KFOR camera with MoK_α radiation, layer-line photographs $hk0$ were obtained, in all only 15 reflections; $hk1$, 11 reflections; and $hk2$, 8 reflections. Apart from the integral extinctions corresponding to the F-Bravais lattice, there were no other detailed indications, and three holohedral groups were possible: $O_h^5 = Fm3m$, $O^3 = F432$, and $T_d^2 = F\bar{4}3m$. The reflection intensities were estimated visually from blackening marks. After extraction of the angular factor LP, the set $|F(hk0)|$ was used to construct the electron-density projection $\sigma(xy)$, with positive signs assigned to all structure amplitudes (Co atom at 000). In the projection, maxima appeared rather clearly along the edges of the elementary cube at a distance of 1.94 Å from the origin; i.e., we again have octahedral coordination about the central Co by five NH_3 groups, to which, with sufficient probability, a sixth N from the NCS group is also attached.

It proved impossible to localize all the atoms of the structure $[Co(NH_3)_5NCS] \cdot (NCS)_2$ because of the limited experimental set of structure amplitudes.

The crystal structure of Co(III) ammines with an inner-sphere thiocyanato group $[Co(NH_3)_5NCS]X_2$, where X = NO_3, Cl, NCS, may formally be described as fluorite-like (CaF_2), i.e., as a face-centered cubic packing of octahedral complex cations, with ions of the second coordination sphere located at the centers of each octant of the cell. The octahedral complex in the three pentaammine rhodanides consists of five NH_3 and one NCS, statistically distributed over the six vertices of an octahedron around Co. Coordination of the NCS group with the central Co(III) occurs through the N atom; i.e., the cobalt ammines studied, with an NCS group in the inner sphere, must be defined as isothiocyanato compounds.

The distance Co(III)–N(NH_3) = Co(III)–N(NCS) = 1.95 ± 0.02 Å corresponds to the sum of the covalent radii ($1.22 + 0.70$ Å) and to the value of the Co(III)–N vector reported in the literature[6].

The thiocyanato group is elongated along the coordinate axes toward the midpoint of the cube edge. The S atoms are not situated exactly at 1/2 1/2 1/2, 1/2 0 0, 0 1/2 0, 0 0 1/2 (the second set of 4-fold positions), but statistically around them in six (24) positions, displaced by 0.69 Å from the 4-fold special points. The NCS group itself is linear; the sequence of bonds Co–N–C–S is determined by a single straight line.

The statistical distribution of five NH_3 groups and one NCS group over the six

vertices of an octahedron, at the center of which is a Co(III) atom, has been established for the first time. In[7], data were published on the statistical distribution of ligands in cobalt ammines containing one and two water molecules in the inner coordination sphere.

Replacement in $[Co(NH_3)_5NCS](NO_3)_2$ of the planar nitrate group NO_3 by the spherically symmetric halogen ion Cl and by the linear asymmetric thiocyanate ion SCN does not lead to a change in the symmetry of the crystal, but only to an increase in the lattice parameters in accordance with the larger sizes of the ions. This may be interpreted as follows: the weak force field inside the complex cation $[Co(NH_3)_5NCS]^{2+}$ permits rotation or statistical behavior of the atomic groups of the second coordination sphere, which leads to an increase in the symmetry of the complex as a whole.

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Note: Figure translations are in progress. See original paper for figures.