CRYSTALLOGRAPHY

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Abstract

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THE CRYSTAL STRUCTURE OF THIOCYANATOPENTAMMINECOBALT NITRATE $[Co(NH_3)_5NCS](NO_3)_2$

The compound $[Co(NH_3)_5NCS](NO_3)_2$ was synthesized by the Werner-Müller method ([1]). Crystals grown from an aqueous solution by slow crystallization at room temperature were regular octahedra of orange-red color. The perfect regularity of the octahedra was also confirmed by a goniometric investigation of 10 crystals. If the initial aim of the X-ray study was to determine the question of through which atom the thiocyanate group is attached to the cobalt atom, then, in connection with the results of the geometrical analysis, there arose the still more important question of the agreement of the octahedral complex of $5NH_3$ and NCS with the cubic symmetry of the whole.

The X-ray investigation—Laue photographs, oscillation and rotation photographs of four layer lines about the 4-fold axis (kfo-programs)—completely confirmed that the crystals belong to the old Laue cubic class

$$O_h = \frac{4}{m}\bar{3}\frac{2}{m} = m3m.$$

Apart from the integral extinctions corresponding to a face-centered Bravais lattice (h, k, l of the same parity), there were no other detailing indications. Thus, the possible Fedorov space groups of symmetry were the symmorphic groups:

$$O_h^5 = Fm3m, \qquad O^3 = F432, \qquad T_d^2 = F\bar{4}3m.$$

The edge of the elementary cube is $a = 10.73 \pm 0.02$ Å. The pycnometrically determined (with evacuation of air) density of the crystals $[Co(NH_3)_5NCS](NO_3)_2$ is $\delta = 1.766$. It follows from this that the elementary cube contains 4 formula units (“molecules”) of the indicated composition.

The smallest multiplicity in all three indicated Fedorov groups is also equal to 4, and all the corresponding positions are special, without parameters; thus, without doubt, the Co atom could be considered to be located at the origin of the cubic cell. The presence of one more system of 4-fold positions in all these

Fig. 1. Weighted projection $P_1(xy)$ $[Co(NH_3)_5NCS](NO_3)_2$ (regions of negative heights are indicated by dashed lines)

Figure 1: Fig. 1. Weighted projection $P_1(xy)$ $[Co(NH_3)_5NCS](NO_3)_2$ (regions of negative heights are indicated by dashed lines)

groups made it possible to suppose that one of the atoms of the thiocyanate radical, most probably S, would be located in these positions. The Co and S atoms are then arranged like Na and Cl in the rock-salt structure. The 20 groups NH_3 can be arranged around 4 Co atoms according to the octahedral law, using 24-fold positions (on the coordinate axes), which are also characteristic of all 3 groups under consideration; these positions are occupied by the N atoms of NH_3 statistically with probability 5/6, and it may be hoped that the remaining 1/6 of the positions will be occupied by the N atoms of the thiocyanate radical. For the 8 groups NO_3, more precisely for the central N atom, the most probable are the 8-fold positions at the centers of all octants of the elementary cube.

All layer-line developments $(0, 1, 2, 3)$ were obtained with Mo radiation. Intensities were estimated with the aid of a blackening-grade scale in relative units and were corrected for the polarization and kinematic factors. The absorption factor was not introduced; the justification for this was the isoperiodicity and relative isometricity of the crystals under ⋯

of insignificant dimensions (0.2 mm). The unaccounted-for temperature factor compensates to some extent for the absorption factor.

The values of $|F|^2$ obtained were used to construct Patterson projections $P_0(xy)$, weighted (conditional) projections $P_n(xy)$, and also linear and plane (Harker) sections through the three-dimensional Patterson function.

According to a feature common to all projections (Fig. 1 reproduces the projection $P_1(xy)$), there were peaks on the edges of the unit cube at a distance of 1.90 Å from

Fig. 1. Weighted projection $P_1(xy)$ $[Co(NH_3)_5NCS](NO_3)_2$
(regions of negative heights are indicated by dashed lines)

the Co atom, corresponding to octahedral coordination around the central atom by five NH_3 addends, to which, probably, the 6th N atom from the NCS group is also attached. The indicated distance corresponds to the sum of the covalent radii and to that value of the Co–N vector which is found in the literature (^{3}-^{5}).

As for the sulfur atom, or more precisely the peak corresponding to the Co –S vector, it is hidden (with an arrangement similar to Na–Cl in the rock-salt structure) on the $h0l$ projection under the repeated origin peak at $\frac{1}{2}00$ and $0\frac{1}{2}0$ (in accordance with the F-lattice), but it appears equally well on the zero Harker section and on two weighted conditional projections $h1l$ and $h2l$, and moreover (on the latter) in different "colors" (two-color symmetry of the conditional projections) at a distance from the Co atom equal to 4.6 Å, which agrees well with both reported distances Co(Ni)—(NC)S = 4.7-4.8 Å, if one takes into account that the sequence of bonds Co–N–C–S need not coincide with a single straight line (^{2},^{5}).

Thus, it must be concluded that the S atoms occupy not particular–parameter-free–positions $m3m$, but are distributed statistically around empty 4-fold positions over 24-fold positions.

It is of interest that the effectively small Z attributable to $\frac{1}{6}$ of an S atom nevertheless leaves this atom almost as visible as the ···

separated (5/6) N atoms. It is probably permissible to assume that the N atom is somewhat "spread out" because of the necessity of sharing three (of 7) of its electrons with the H atoms from the NH_3 group. Such a situation would hardly obtain if the atom nearest to Co were S.

Thus, the Patterson projections of the structure with the heavy Co atom at the origin lead to the conclusion that the octahedral complex in the present pentaamminerhodanide consists of 5 NH_3 groups and one NCS group, statistically distributed over the 6 vertices of an octahedron around Co. The NCS group itself is elongated along the coordinate axes toward the center of the edge a. (With respect to Co atoms at the centers of the faces of the cube, the NCS group may also be elongated toward the center of the elementary cube.)

The S atoms are located not exactly in the positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$, but statistically in 6 positions around them, displaced by 0.9 Å.

The Co–N(H_3) distance is 1.90-1.95 Å. The distance along the edge is 4.6 Å, as against the usually indicated 4.7-4.8 Å; but it is not clear whether these three bonds Co–N–C–S will lie on one straight line.

On the NO_3 groups and the second coordination sphere. If the NO_3 complex is considered as a whole, then 8-fold positions at the centers of the 8 octants of the cell, with symmetries O_h and O, seem suitable for it. The uncertainty (statistical character) of the positions of the C and S atoms in the NCS group also makes uncertain the positions of the O atoms around N, but the N atoms have the possibility of being at the points $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, etc., which also seems to follow from the $P_0(xy)$ projection. However, on the conditional (weighted) $h1l$ projection, the very sharp peak $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ is split into 4 peaks surrounding the point $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ at the vertices of a tetrahedron (different "colors" on the conditional $h1l$ projection). Comparison of the colors (the signs + and –) indicates that if the N atom statistically occupies 32-fold positions, then it is situated (as should be expected) farther from Co and closer to the S atom. The Co–N(O_3) distance is obtained as 5.3 Å, which appears to agree well with the sum: "radius of the first sphere" (2.0+1.3) plus the radius of the flattened NO_3 group (1.3+0.6). The distance (O_3)N–S (the center of an octahedron of six $\frac{1}{6}$S) is $\sim$ 4.0 Å (1.3+0.6+1.9=3.8).

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