CRYSTAL STRUCTURE OF ISOTHIOCYANATO-DINITRO-(ETHYLENEDIAMINE)-AMMINECOBALT(III)

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Abstract

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CRYSTAL STRUCTURE OF ISOTHIOCYANATO-DINITRO-(ETHYLENEDIAMINE)-AMMINECOBALT(III)

When ammonium thiocyanate acts on trinitro-(ethylenediamine)-amminecobalt(III), one nitro group in the latter is replaced by a thiocyanato group (⁀1). According to the regularity of the trans influence, in the product obtained the NCS group should be in the trans position to one nitro group and in the cis position to the other nitro group. The same product $[Co(NCS)(NO_2)_2enNH_3]$ was also obtained by the action of NH_4NCS on chlorodinitro-(ethylenediamine)-amminecobalt(III), which in turn is obtained from trinitro-(ethylenediamine)-amminecobalt(III) by the action of concentrated hydrochloric acid. In (⁀2) it was shown that in the chlorodinitro compound the chlorine atom is in the trans position with respect to the nitro group. Thus, the chemical data confirm the structure of the thiocyanato-dinitro compound expected on the basis of the regularity of the trans influence. However, the possibility of isomerization, which occurs rather readily in Co(III) compounds, somewhat reduces confidence in the results of chemical investigations. In order to obtain direct data on the configuration of the thiocyanato-dinitro compound, its crystal structure was determined.

The product studied was obtained by the method described in (⁀1) and was recrystallized from a hot aqueous solution.

Two modifications of $[Co(NCS)(NO_2)_2 \times enNH_3]$ crystals were found: monoclinic, with parameters $a = 8.34 \pm 0.02$, $b = 10.42 \pm 0.02$, $c = 12.49 \pm 0.03$ Å, $\beta = 104^\circ \pm 30'$, and orthorhombic, $a = 16.26 \pm 0.05$, $b = 10.68 \pm 0.02$, $c = 24.65 \pm 0.09$ Å. The orthorhombic cell is approximately equal in volume to four monoclinic cells. The following relation is established between the parameters of the two cells: $a_p \approx 2a_m \sin\beta$, $b_p \approx b_m$, $c_p \approx 2c_m$.

Monoclinic crystals were selected as the object of investigation. Subsequently it turned out that under the action of X-rays they are not very stable—after approximately 300 h of exposure the intensity of the rays diffracted by them decreases so much that the crystals become unsuitable for further photography. The reflections on the Lauegrams, sharp at the beginning of the photography,

gradually become diffuse as the exposure increases. The external form and the luster of the crystal faces do not undergo noticeable changes.

The experimental material consisted of layer-line developments $h0l$–$h2l$, obtained in an RFOR X-ray goniometer (Mo radiation, $\sin\vartheta/\lambda \leq 0.65$ Å^{-1}) with specimens having linear dimensions of about $0.35 \times 0.1 \times 0.15$ mm^3, and $0kl$ and $1kl$, taken with specimens $1.0 \times 0.15 \times 0.2$ mm^3. The systematic extinctions determined the Fedorov group $P2_1/c$. There are 4 formula units of the above composition per unit cell. The intensities were estimated visually from blackening marks with a scale step of $\sqrt[4]{2}$. In converting the intensities into structure factors, the kinematic and polarization factors were taken into account; no absorption correction was introduced.

The structure was solved from projections of the Patterson function and electron density on the principal planes (010) and (100). For localization

crystallochemical standards were used for some atoms, since a large number of overlaps is observed on the syntheses $\sigma(xz)$ and $\sigma(yz)$. The structure was refined by the method of least squares using programs developed at the Computing Center of the Branch of the Institute of Chemical Physics of the Academy of Sciences of the USSR ([3]). Initially, a refinement procedure based on two independent arrays of structure amplitudes ([4]) was applied. The first array included 367 nonzero reflections from layer-line scans $h0l$—$h2l$, the second–235 reflections from layers $0kl$ and $1kl$.

Six cycles of refinement of positional parameters and of the overall thermal factor were carried out for each array. At the final stages the discrepancy factors were 0.16 for the first array and 0.12 for the second, with $B_{hkl} = 3.54$ and $B_{Hkl} = 3.49$ Å^2.

Since for some atoms the values of the common z-coordinate obtained from the two arrays differed substantially ($\Delta z >> 0.1$ Å), it was necessary to proceed to refinement of the structure using a single combined array. The experimental structure factors from all 5 layer-line scans were brought to a single scale by comparing them with the calculated values. The array consisted of 535 amplitudes of nonzero reflections not related by symmetry. In refining the structure from individual layer-line scans, corrections for bringing F_{exp} to the absolute scale were refined only for the 0th, 1st, and 2nd layer lines along the b axis. At the final stage, individual isotropic temperature corrections to the common temperature factor were refined. The final discrepancy factor is 0.134. The obtained coordinates of the basis atoms are given in Table 1, and the principal intracomplex interatomic distances and bond angles–in Table 2.

Fig. 1. Configuration of the complex $[Co(NCS)(NO_2)_2enNH_3]$

Table 1

Coordinates and isotropic temperature factors of the basis atoms

Atom	x/a	y/b	z/c	B_j
Co	0.302	0.115	0.143	3.0
S	0.240	−0.326	0.057	4.6
O_1	0.209	0.369	0.130	7.2
O_2	0.459	0.343	0.185	6.4
O_3	0.383	0.170	−0.055	4.8
O_4	0.136	0.112	−0.078	5.6
N_1	0.321	0.299	0.156	5.8
N_2	0.538	0.106	0.155	3.4
N_3	0.270	0.137	−0.017	3.6
N_4	0.067	0.125	0.135	3.0
N_5	0.332	0.089	0.305	4.3
N_6	0.291	−0.069	0.124	3.5
C_1	0.031	0.137	0.248	4.0
C_2	0.167	0.055	0.323	3.9
C_3	0.257	−0.171	0.096	3.0

Table 2

Principal interatomic distances and some bond angles in the complex $[Co(NCS)(NO_2)_2enNH_3]$

Atoms	Å	Atoms	Å
$Co–N_1$	1.93	$C_1–C_2$	1.54
$Co–N_2$	1.94	$N_1–C_3$	1.13
$Co–N_3$	1.96	$C_3–S$	1.68
$Co–N_4$	1.94	$N_1–O_1$	1.17
$Co–N_5$	2.00	$N_1–O_2$	1.21
$Co–N_6$	1.93	$N_3–O_3$	1.20
$N_4–C_1$	1.52	$N_3–O_4$	1.22
$N_5–C_2$	1.49		
degrees		degrees	
$N_4–Co–N_5$	86	$Co–N_6–C_3$	166
$Co–N_4–C_1$	112	$N_6–C_3–S$	170
$Co–N_5–C_2$	107	$O_1–N_1–O_2$	119
$N_4–C_1–C_2$	103	$O_3–N_3–O_4$	120
$N_5–C_2–C_1$	110		

Figure 1 shows the complex isothiocyanatodinitro-(ethylenediamine)-amminecobalt. The Co atom coordinates six N atoms in a slightly distorted octahedron. The nitro groups occupy *cis* positions with respect to one another, and the thiocyanato group is in the *trans* position to one of them. This result

Fig. 2. Projections of the structure onto the planes (010) (a) and (100) (b)

Figure 1: Fig. 2. Projections of the structure onto the planes (010) (a) and (100) (b)

confirms the conclusions drawn on the basis of chemical investigations and agrees with the regularity of the trans influence. Distances

Co–N lie in the range 1.93-2.00 Å; the angles between neighboring Co–N bonds differ only slightly from 90°, the largest deviation from a right angle being in the intrachelate angle N_4–Co–N_5, equal to 86°. The ethylenediamine molecule has the gauche configuration; the interatomic distances and valence angles in the molecule agree with literature data. The standard ones with respect to structure are the nitro groups.

Fig. 2. Projections of the structure onto the planes (010) (*a*) and (100) (*b*)

The thiocyanato group is attached to the cobalt atom through the nitrogen atom, as in other cobalt(III) ammines (5). Thus, the compound in question is isothiocyanatodinitro-(ethylenediamine)-amminecobalt(III). The configuration of the thiocyanato group deviates somewhat from linear–the angle at the C atom is 170°. A deviation from linearity is also observed in the sequence of bonds Co–N_6 and N_6–C_3; the angle Co–N_6–C_3 = 166°.

The structure consists of monomeric complexes. The distinctive feature of their packing is that (Fig. 2) the nearest environment of the thiocyanato group is composed mainly of O atoms of the nitro groups of neighboring complexes. It is possible that this is the reason for the observed instability of the crystals under study.

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