CRYSTAL STRUCTURES OF COBALT(III) DIOXIMINES WITH INNER-SPHERE SELENOCYANATO AND THIOCYANATO GROUPS

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Abstract

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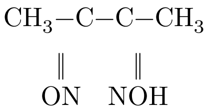
I. D. SAMUS, Academician N. V. BELOV

CRYSTAL STRUCTURES OF COBALT(III) DIOXIMINES WITH INNER-SPHERE SELENOCYANATO AND THIOCYANATO GROUPS

$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$ AND

$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$

In (^{1,2}) the results were reported of a goniometric and preliminary X-ray structural study of crystals of $NH_4[Co(DH)_2(XCN)_2] \cdot 3H_2O$ (X = Se, S), where DH is the dimethylglyoximate ion



$$\begin{array}{cccc} \mathrm{CH_3}- & \mathrm{C} & - \; \mathrm{C} & -\mathrm{CH_3} \\ & \| & \| & \\ & \mathrm{ON} & \mathrm{NOH} & \end{array}$$

The refined parameters of the monoclinic cell (KFOR with a NaCl standard, unfiltered Mo radiation, rotation about y and z) are:

$$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O: \quad a = 10.10 \pm 0.03\ \text{Å}, \quad b = 12.25 \pm 0.02\ \text{Å},$$

$$c = 8.33 \pm 0.03\ \text{Å}; \quad \beta = 95°00'; \quad \text{space group } P2_1/n; \quad Z = 2; \quad \rho = 1.75\ \text{g/cm}^3;$$

$$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O: \quad a = 10.01 \pm 0.03\ \text{Å}, \quad b = 12.06 \pm 0.02\ \text{Å},$$

$$c = 8.50 \pm 0.03\ \text{Å}; \quad \beta = 95°20'; \quad \text{space group } P2_1/n; \quad Z = 2; \quad \rho = 1.53\ \text{g/cm}^3.$$

Fig. 1. Projection yz of the electron density of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$. Contour lines every 3 e/Å^2. Dashed lines correspond to 3 e/Å^2.

Figure 1: Fig. 1. Projection yz of the electron density of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$. Contour lines every 3 e/Å^2. Dashed lines correspond to 3 e/Å^2.

Fig. 1. Projection yz of the electron density of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$. Contour lines every 3 e/Å^2. Dashed lines correspond to 3 e/Å^2.

The intensities were estimated from blackening marks with a step of $\sqrt[4]{2}$; for the brightest reflections, films with multiple exposures were used. In selecting the amplitudes, only the angular factor LP was taken into account, without correction for absorption.

Initial information on the structure of the Co dimethylglyoximates was provided by Patterson projections. The principal interpretation was carried out on crystals of $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$; refinement was performed from three-dimensional experimental data independently for both compounds.

From maps (perpendicular to the y axis) of sections of the three-dimensional electron-density distribution constructed for $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$, using signs calculated from the coordinates of the heavy atoms Se and Co, the coordinates of the light atoms of the complex anion were obtained. With respect to ammonium ions and water molecules, it was necessary to assume that two N from NH_4 and two O from H_2O statistically occupy one set of general fourfold positions.

The number of reflections used in calculating projections and the three-dimensional electron-density distribution for $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$ was 439. Reduction of the $F(hkl)_{\text{exp}}$ array to the absolute scale was carried out by comparing the moduli of the observed structure amplitudes with those calculated from the coordinates of Co and Se. When the values of $F_{\text{r}}(hkl)$, calculated from the coordinates found for all atoms, were compared with those calculated from the atoms Co (at the origin of coordinates) and Se, it was found that, of 439 reflections, 13 reflections change sign, i.e., $\sim 3\%$. Refinement ([3,4]) of all positional parameters of the structure and of individual isotropic corrections led to an R-factor of 10.2% at $K = 1.07$ and $B = 2.69$ Å^2.

The final coordinates of the basic atoms of $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$ are given in Table 1 (accuracy according to Weinstein–Porai-Koshits ([5,6]): ~ 0.016 Å for C, N, O and ~ 0.002 Å for Se).

Refinement of the structure of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ was carried out by the same method (least squares), using individual isotropic temperature corrections. After the seventh stage of refinement the discrepancy factor R_{hkl} decreased from 25 to 11.6% for 479 independent nonzero reflections. The structural parameters of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ are presented in Table 1. (The projection of the electron density $\sigma(yz)$ is given in Fig. 1.)

The elements of the two crystal structures should be regarded as octahedral complex anions $[Co(DH)_2(XCN)_2]^-$ (inner coordination sphere), NH_4^+ cations, and H_2O molecules. Two NH_4^+ ions (more precisely, N atoms) and six H_2O molecules (O atoms) are statistically distributed over two common fourfold positions. Figure 2 shows the xy projection of the structure of $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$. The slightly distorted coordination octahedron around Co is formed by four N atoms from two dimethylglyoxime residues and by two S (respectively Se) atoms from thiocyanato-

Table 1

Coordinates of atoms and isotropic temperature factors B_j for $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$ and $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$

Atoms	x/a	y/b	z/c	B_j, Å^2	Atoms	x/a	y/b	z/c	B_j, Å^2
$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$					$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$				
Co	0.0000	0.0000	0.0000	2.17	Co	0.0000	0.0000	0.0000	3.15
Se	0.1474	0.1356	0.1174	2.64	S	0.1467	0.1342	0.1076	2.98
O_I	−0.0388	−0.0839	0.3061	2.41	O_I	−0.0291	−0.0876	0.3085	3.53
O_{II}	−0.1445	0.1644	−0.1742	3.25	O_{II}	−0.1605	0.1647	−0.1731	3.54
O_{III} (H_2O)	0.4464	0.1363	0.4220	4.24	O_{III} (H_2O)	0.4393	0.1328	0.4216	4.91
O_{IV} (H_2O)	0.0725	0.4201	0.1813	3.30	O_{IV} (H_2O)	0.0745	0.4204	0.1939	4.07
N_I	−0.0857	−0.0077	0.2008	2.92	N_I	−0.0769	−0.0147	0.2043	2.49
N_{II}	−0.1316	0.1175	−0.0347	2.86	N_{II}	−0.1373	0.1190	−0.0361	2.24
N	0.3764	0.1372	−0.0929	5.27	N	0.3759	0.1174	−0.0812	4.70
C	0.2855	0.1406	−0.0048	4.37	C	0.2782	0.1299	−0.0017	3.15
C_I	−0.1651	0.0598	0.2415	2.73	C_I	−0.1663	0.0557	0.2410	3.82
C_{II}	−0.2016	0.1245	0.0978	2.68	C_{II}	−0.1935	0.1281	0.0945	4.04
C_{III} (CH_3)	−0.2196	0.0469	0.3987	2.11	C_{III} (CH_3)	−0.2236	0.0529	0.3939	4.84
C_{IV} (CH_3)	−0.3062	0.2113	0.0850	3.33	C_{IV} (CH_3)	−0.3054	0.2125	0.0847	3.21

and selenocyanato groups located in the trans position. The distortion of the octahedron is caused by the bidentate character of the dimethylglyoxime ligands. These radicals lie in one plane, being held together by strong intramolecular hydrogen bonds. The mean deviation of the atoms from the plane drawn through Co and the atoms of the DH grouping is (l.s.) 0.04 Å. The interatomic distances and valence angles in $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ and $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$, calculated from the final coordinates (the accuracy of the determination of the angles according to Darlow (^{7}) is 1–2°), are given in Table 2.

The bond lengths and valence angles in dimethylglyoxime agree satisfactorily with the values for $Ni(DH)_2$ (^{8}), $Pt(DH)_2$ (^{9}), and $[Co(DH)_2(NH_3)_2] \cdot NO_3$ (^{10}). The O—H···O distance is shortened to 2.44-2.49 Å.

In all the Co complex compounds with a thiocyanato group in the inner sphere that have been investigated structurally, the SCN group is attached to cobalt through the N atom.

In the dioximes the Co atom attaches selenocyanato and thiocyanato groups through the chalcogen. The obtained distance Co(III)—Se = 2.383 ± 0.002 Å agrees well with the sum of the covalent radii, 1.22 Å (Co) + 1.17 Å (Se) (^{11}). The found Co(III)—S = 2.316 ± 0.004 Å somewhat exceeds the ordinary length 2.26 Å, calculated on the basis of the covalent radii (1.22 Å (Co) + 1.04 Å (S)). The valence angle between the Co–S bond line and the axis of the thiocyanato group is 105°, and between Co–Se and the axis of the selenocyanato group, 106°. The proximity of the angle Co—S(Se)—C to 90° and the weakening of the S(Se)—C bond in comparison with a double bond may be associated with the fact that the coordination covalent bond Co—S(Se) is formed at the expense of the π-electron cloud of the SCN group and, correspondingly, of the SeCN group. A probable reason for the increase of the angle between the Co—S(Se) bonds and the thiocyanato (selenocyanato) group to 105-106° instead of 90° is steric hindrance in contacts of the C atom from the group

Table 2

Interatomic distances and valence angles in the structures $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ and $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$

Distances, Å	Angles, deg.	Distances, Å	Angles, deg.
$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$	$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$	$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$	$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$
Co—S 2.316$\pm$0.004	Co—S—C 105	Co—Se 2.383	Co—Se—C 106
Co—N_I 1.97$\pm$0.01	S—C—N 174	Co—N_I 1.95	Se—C—N 179
Co—N_{II} 1.99$\pm$0.01	Co—N_I—O_I 121	Co—N_{II} 1.96	Co—N_I—O_I 116
S—C 1.68$\pm$0.01	Co—N_I—C_I 120	Se—C 1.80	Co—N_I—C_I 124
C—N 1.25$\pm$0.02	C_I—N_I—O_I 120	C—N 1.22	C_I—N_I—O_I 119
N_I—O_I 1.31$\pm$0.01	N_I—C_I—C_{II} 105	N_I—O_I 1.34	N_I—C_I—C_{II} 106
N_I—C_I 1.29$\pm$0.02	N_I—C_I—C_{III} 122	N_I—C_I 1.22	N_I—C_I—C_{III} 118
C_I—C_{II} 1.52$\pm$0.02	Co—N_{II}—O_{II} 121	C_I—C_{II} 1.46	Co—N_{II}—O_{II} 118

Fig. 2. Projection of the structure $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ along [001]

Figure 2: Fig. 2. Projection of the structure $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ along [001]

Distances, Å	Angles, deg.	Distances, Å	Angles, deg.
$C_{I}—C_{III}$ 1.47$\pm$0.02	$Co—N_{II}—C_{II}$ 107	$C_{I}—C_{III}$ 1.48	$Co—N_{II}—C_{II}$ 106
$N_{II}—O_{II}$ 1.29$\pm$0.01	$C_{II}—N_{II}—O_{II}$ 133	$N_{II}—O_{II}$ 1.30	$C_{II}—N_{II}—O_{II}$ 133
$N_{II}—C_{II}$ 1.30$\pm$0.02	$N_{II}—C_{II}—C_{I}$ 126	$N_{II}—C_{II}$ 1.36	$N_{II}—C_{II}—C_{I}$ 121
$C_{II}—C_{IV}$ 1.51$\pm$0.02	$N_{II}—C_{II}—C_{IV}$ 113	$C_{II}—C_{IV}$ 1.49	$N_{II}—C_{II}—C_{IV}$ 114
$O_{I} \cdots O'_{II}$ 2.49$\pm$0.01	$C_{I}—C_{II}—C_{IV}$ 120	$O_{I} \cdots O'_{II}$ 2.44	$C_{I}—C_{II}—C_{IV}$ 125
	$C_{II}—C_{I}—C_{III}$ 133		$C_{II}—C_{I}—C_{III}$ 134
	$N_{I}—Co—N_{II}$ 83		$N_{I}—Co—N_{II}$ 82
	$N_{I}—O_{I}—O'_{II}$ 101		$N_{I}—O_{I}—O'_{II}$ 103
	$N_{II}—O_{II}—O'_{I}$ 100		$N_{II}—O_{II}—O'_{I}$ 102
	$S—Co—N_{I}$ 90		$Se—Co—N_{I}$ 89

SCN (SeCN) and N from the DH grouping (the distance of 2.88 Å between the C atom from the SCN group and N from the dioxime grouping is less than the sum of the intermolecular radii, 1.72 Å (C) + 1.57 Å (N), by 0.41 Å). The results of the determination of the atomic structure of cobalt(III) dioximes with inner-sphere selenocyanato and thiocyanato groups confirm the supposition of A. V. Ablov [12] that in Co-dioximes, where the thiocyanato group has the stronger trans effect, the bond of the latter with Co is effected through S.

Fig. 2. Projection of the structure $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ along [001]

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Kishinev Polytechnic Institute
named after S. Lazo

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CITED LITERATURE

1. I. D. Samus' , *Izv. AN MSSR*, No. 10 (88) (1961).
2. A. V. Ablov, I. D. Samus' , *DAN*, **146**, 1071 (1962).
3. B. L. Tarnopol' skii, V. I. Andrianov, *ZhSKh*, **4**, 433 (1963).
4. B. L. Tarnopol' skii, *ZhSKh*, **4**, 892 (1963).
5. B. K. Vainshtein, *ZhETF*, **27**, 44 (1954).
6. M. A. Porai-Koshits, *Practical Course of X-ray Structural Analysis*, 2, Moscow, 1960, p. 600.
7. S. F. Darlow, *Acta Crystallogr.*, **13**, 683 (1960).
8. L. E. Godycki, R. E. Rundle, ibid., **6**, 487 (1953).
9. E. Frasson, C. Panattoni, R. Zanetti, ibid., **12**, 1027 (1959).
10. K. S. Viswanathan, N. R. Kunchur, ibid., **14**, 675 (1961).
11. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Ithaca, 1960.
12. A. V. Ablov, N. M. Samus' , M. S. Popov, *DAN*, **106**, 665 (1956).

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

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