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The Crystal Structure of Bis(ethylenediamine)isothiocyanatonitrocobalt(III) Thiocyanate $[Co(NCS)NO_2(en)_2]SCN$

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The crystal structure of *trans*-bis(ethylenediamine)isothiocyanatonitrocobalt(III) thiocyanate has been determined. The crystals are monoclinic with $a = 16.343(13)$ Å, $b = 16.026(7)$ Å, $c = 11.146(3)$ Å, $\beta = 110.28(4)°$, $V = 2738$ Å^3, $Z = 8$, space group $C2/c$.

Least squares refinement of the structure based on 1970 reflections, gave an R-value of 0.077. The bis(ethylenediamine)isothiocyanatonitrocobalt(III) ions are arranged in closepacked layers which are separated from each other by the thiocyanate ions. The cobalt atoms are octahedrally coordinated by six nitrogen atoms with the bond distances Co—N (to NO_2) 1.914(7) Å, Co—N (to NCS) 1.922(7) Å, and Co—N (to en) 1.959—1.966(7) Å.

In connection with studies of the conversion of nitro and nitrito compounds Adell [1] prepared the two salts $[Co(NCS)NO_2(en)_2]SCN$ and $[Co(NCS)NO_2(en)_2]ClO_4$. When the salts were exposed to sunlight the perchlorate was converted to the nitrito form while the thiocyanate was not. In order to examine whether there are any sterical reasons for this the crystal structure of the thiocyanate has been determined.

STRUCTURE DETERMINATION

Using a thin needle-shaped crystal the intensities of the $hk0 - hk14$ reflections were recorded by a Philips Pailred automatic single crystal diffractometer with Mo$K\alpha$ radiation monochromatized with a graphite crystal. The intensities were corrected for Lorentz and polarization effects using the program DATAP1. The cell dimensions were obtained from powder diffraction photographs taken with a Guinier focusing camera with Cu$K\alpha$ radiation, using lead nitrate ($a = 7.8566$ Å)[2] as an internal standard, and refined by the method of least squares using the program POWDER. Bis(ethylenediamine)-isothiocyanatonitrocobalt(III) thiocyanate was found to be monoclinic with $a = 16.343(13)$ Å, $b = 16.026(7)$ Å, $c = 11.146(3)$ Å, $\beta = 110.28(4)°$, and $V = 2738$ Å^3.

The following reflection conditions were noted: hkl: $h + k = 2n$ and $h0l$: $l = 2n$. Possible space groups $C2/c$ or Cc. The calculated density for a unit cell containing eight formula units is 1.65 g cm^{-3}.

The parameters of the cobalt atoms were deduced from the three-dimensional Patterson function $P(uvw)$ calculated with the program DRF. The other atoms were determined from three-dimensional electron density maps. One of the thiocyanate ions was found along the two-fold axis of $C2/c$ [4(e)] but the other had to be placed perpendicular to and across the axis. This indicates either that this latter thiocyanate ion is statistically orientated in two directions or that the space group is Cc.

The structure was refined by least squares using the program BLOCK. The atomic scattering factors used were those calculated by Doyle and Turner [3] and the structure factors were weighted according to Cruickshank [4] with $a = 80.0$ and $c = 0.005$. When the refinement was performed in the space group Cc the temperature factor of the sulfur atom of the second thiocyanate ion got a high value while the temperature factor of the nitrogen atom was low. This was taken as an indication that the space group was the centric $C2/c$ with the thiocyanate ion statistically distributed in two

Table 1. Final atomic parameters for $[Co(NCS)NO_2(en)_2]SCN$. The anisotropic temperature factor is exp $\{-(h^2(a^*)^2u_{11}+k^2(b^*)^2u_{22}+l^2(c^*)^2u_{22}+l^2(c^*)^2u_{33}+2hka^*b^*u_{12}+2hla^*c^*u_{13}+2klb^*c^*u_{23})\}$. The standard deviations of u_{ij} are $(3-4)\times 10^{-4}$ for Co and $(1-21)\times 10^{-3}$ for other atoms.

Atom	x	y	z	$u_{ij}\times 10^3$ u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
S(1)	0.0	0.0495(3)	0.75	312	33	428	0	341	0
C(1)	0.0	0.1497(10)	0.75	75	55	68	0	48	0
N(1)	0.0	0.2207(8)	0.75	93	43	57	0	28	0
S(2)	0.0829(3)	0.3493(3)	0.3289(6)	35	98	101	−10	14	−39
C(2)	0.0140	0.3493	0.2634	83	87	137	12	59	1
N(2)	0.0829	0.3493	0.3289	117	70	58	17	70	0
Co	0.24784(7)	0.11815(6)	0.23307(10)	27	18	28	0	13	1
S(3)	0.16592(13)	0.13955(13)	0.59582(21)	44	33	37	2	21	−4
C(3)	0.1983(4)	0.1333(4)	0.4730(8)	30	19	36	6	14	5
N(3)	0.2204(4)	0.1283(4)	0.3867(7)	41	33	40	7	21	3
N(4)	0.1920(5)	0.2270(4)	0.1781(7)	44	28	36	5	11	5
C(4)	0.1023(7)	0.2142(7)	0.0835(11)	46	50	64	5	10	10
C(5)	0.0654(6)	0.1381(7)	0.1232(13)	31	50	89	5	15	11
N(5)	0.1321(4)	0.0701(4)	0.1463(7)	26	33	51	−8	13	−4
N(6)	0.3023(4)	0.0089(4)	0.2900(7)	34	28	34	−2	6	−1
C(6)	0.3910(8)	0.0203(7)	0.3768(18)	60	32	165	11	−10	14
C(7)	0.4292(7)	0.0944(7)	0.3576(15)	44	45	123	1	16	15
N(7)	0.3639(4)	0.1652(4)	0.3214(8)	21	35	53	−2	11	−5
N(8)	0.2750(4)	0.1105(4)	0.0796(7)	49	35	36	−6	25	1
O(1)	0.3115(5)	0.1679(5)	0.0486(8)	113	75	64	−34	52	11
O(2)	0.2529(6)	0.0512(5)	0.0119(9)	199	65	89	−63	105	−47

directions across the two-fold axis. The refinement of the ion was then performed so that only the coordinates of the sulfur atom were refined while the nitrogen atom was given the same coordinates as the sulfur atom. The coordinates of the carbon atom were reset so that the ratio between the bond distances N−C and C−S was the same as in the other thiocyanate ion. After the introduction of anisotropic thermal parameters the reliability index $R=\sum||F_o|-|F_c||/\sum|F_o|$ converged to 0.077. The resulting parameters are given in Table 1. A list of observed and calculated structure factors can be obtained from the author on request.

DESCRIPTION OF THE STRUCTURE

The complex ion $[Co(NCS)NO_2(en)_2]^+$ is shown in Fig. 1, and the unit cell in Fig. 2 drawn with ORTEP. Bond distances and bond angles are given in Table 2, together with their

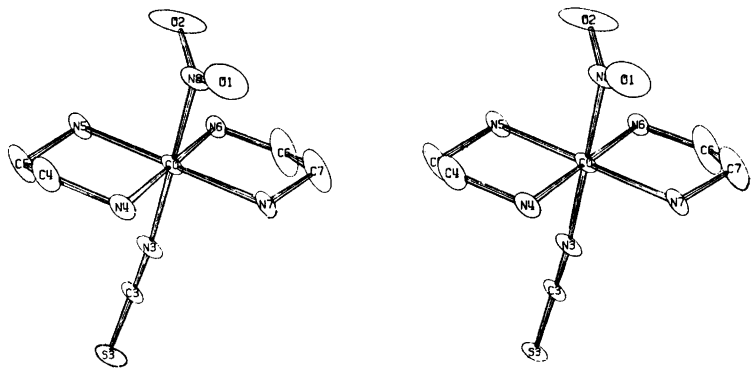

Fig. 1. A stereoscopic view of the ion $[Co(NCS)NO_2(en)_2]^+$.

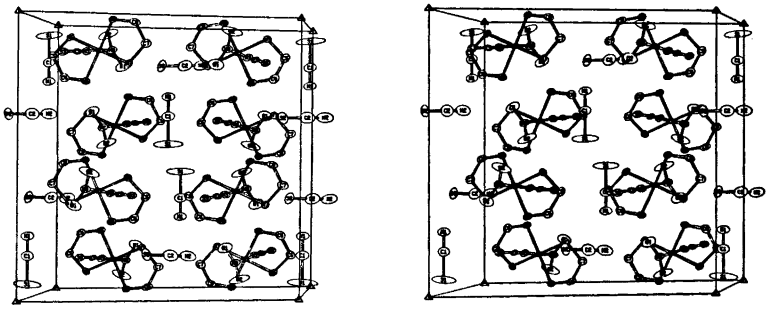

Fig. 2. A stereoscopic view of the structure.

Table 2. Bond distances and angles in $[Co(NCS)NO_2(en)_2]SCN$.

Distance (Å)	
Co – N(8)	1.914(7)
Co – N(3)	1.922(7)
Co – N(5)	1.959(7)
Co – N(7)	1.960(7)
Co – N(4)	1.965(7)
Co – N(6)	1.966(7)
N(3) – C(3)	1.141(11)
C(3) – S(3)	1.633(8)
N(4) – C(4)	1.493(13)
C(4) – C(5)	1.494(15)
C(5) – N(5)	1.498(12)
N(6) – C(6)	1.449(16)
C(6) – C(7)	1.393(17)
C(7) – N(7)	1.514(13)
N(8) – O(1)	1.210(11)
N(8) – O(2)	1.189(11)
S(1) – C(1)	1.606(17)
C(1) – N(1)	1.137(21)
Angle(°)	
N(4) – Co – N(5)	86.0(3)
N(4) – Co – N(7)	94.5(3)
N(5) – Co – N(6)	93.5(3)
N(6) – Co – N(7)	86.0(3)
Co – N(3) – C(3)	175.3(6)
N(3) – C(3) – S(3)	179.3(7)
Co – N(4) – C(4)	109.5(6)
N(4) – C(4) – C(5)	107.5(9)
C(4) – C(5) – N(5)	107.4(8)
C(5) – N(5) – Co	108.7(6)
Co – N(6) – C(6)	109.9(6)
N(6) – C(6) – C(7)	113.7(12)
C(6) – C(7) – N(7)	111.6(9)
C(7) – N(7) – Co	108.4(6)
The other angles round Co are 88.6 – 91.0° or 178.8 – 179.3°.	

standard deviations. The cobalt atom is octahedrally coordinated by the nitrogen atoms of the nitro and isothiocyanato groups in *trans* position and the nitrogen atoms of two ethylenediamine groups. The Co – N bond distances are 1.914(7) Å (to NO_2), 1.922(7) Å (to NCS), and 1.959 – 1.966(7) (to en). The bond distance. C6 – C7 in one ethylenediamine group is rather short, 1.393(17) Å. The explanation of this is probably that the refined coordinates of the carbon atom C6 are the mean values of two possible positions of the atom. This is indicated by its large anisotropic temperature movement and also by the fact that the bond angles involving C6 are larger than other bond angles in the ethylenediamine groups. Very large anisotropic temperature movements are also shown by the atoms of the thiocyanate ion lying along the two-fold axis, especially by the sulfur atom S1.

The structure may be visualized as close packed layers of bis(ethylenediamine)isothio-

Table 3. Packing distances (Å) less than 3.5 Å in $[(Co(NCS)NO_2(en)_2]SCN$.

O(1) – N(4)	3.02
O(1) – C(4)	3.03
O(1) – O(1)	3.26
O(2) – N(3)	3.08
O(2) – C(3)	3.16
O(2) – N(6)	3.01
O(2) – C(6)	3.32
N(7) – N(1)	3.19
N(6) – S(3)	3.46
N(5) – S(3)	3.48
N(5) – S(1)	3.38
N(4) – N(2)	3.45

cyanatonitrocobalt(III) ions parallel to the plane [100] at $x = 0.25$ and $x = 0.75$. The packing distances given in Table 3 indicate that there might be weak hydrogen bonds within the layers. The shortest distances between an oxygen atom and a nitrogen atom of an other complex ion are 3.01 – 3.02 Å. The thiocyanate ions are situated in the space between these layers. This investigation was carried out to see if there are any sterical reasons for the observed inability of the nitro group to be converted to the nitrito form when exposed to sunlight. There do not seem to be any sterical obstacles to such a conversion. The oxygen-nitrogen distances indicating hydrogen bonds are longer than in, *e.g.*, $[CoNO_2(NH_3)_5]Cl_2$[5] for which this conversion has been observed.

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