The Crystal Structure of Cobalt(II) Thiocyanate Trihydrate

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The title compound crystallizes in a monoclinic cell with dimensions $a = 12\cdot490$ (2), $b = 6\cdot024$ (1), $c = 10\cdot740$ (2) Å and $\beta = 90\cdot49$ (1)°. The space group is $C2/c$. It has four $[(SCN)_2Co(H_2O)_2].H_2O$ formula units in the cell. The cobalt atom lies at a symmetry centre surrounded by symmetrically related pairs of water molecules, nitrogen and sulphur atoms. Another water molecule lies on a twofold axis. The final R value is 0·03 for a total of 1091 observed Mo data. The NCS group has the normal characteristic values: $N-C = 1\cdot160$ (3), $C-S = 1\cdot664$ (2) Å and $N-C-S = 179\cdot20$ (2)°. Co–N–C–S–Co links with bidentate NCS are present. The sulphur atom and the water molecules are involved in a hydrogen-bonding network.

Introduction

In the course of an investigation of several compounds of Co^{II} complexes with the thiocyanate ion, it was found that there was some disagreement in the literature concerning the number of bound water molecules, using analogous methods (Pascal, 1963; Cotton & Francis, 1971; *Comprehensive Inorganic Chemistry*, 1973). There are various recent studies being performed on complex compounds of transition metals including the thiocyanate group, though nothing has been found on its cobalt salt. This lack of information was the starting point for the undertaking of the crystallographic study of cobalt(II) thiocyanate trihydrate.

Experimental

Cobalt thiocyanate was obtained by double decomposition from equivalent solutions of barium thiocyanate and cobalt(II) sulphate. Barium sulphate is precipitated and the thiocyanate solution is concentrated by heating. The compound then crystallizes from the water solution by slow evaporation at room temperature in the form of purple-reddish single crystals. Chemical analysis indicated that these crystals are the trihydrate salt. The crystals decompose in the air, losing water and turning a blue colour. Hence they were sealed into Lindemann capillaries for X-ray analysis and during data collection no variation was detected in the three monitored standard reflexions. The crystal data are given in Table 1.

A crystal approximately $0\cdot3 \times 0\cdot4 \times 0\cdot3$ mm was used on a Philips PW 1100 single-crystal diffractometer. The lattice constants were obtained from the settings of twelve reflexions and their Friedel pairs. 1170 intensities were collected in the $\omega/2\theta$ scan mode, within 2 and 30° in θ, with graphite monochromatized Mo $K\alpha$ radiation. Of these reflexions 79 were considered as

Table 1. *Crystal data*

Standard deviations, given in parentheses, refer to the least significant digit.

$(SCN)_2Co^{II}.3H_2O$	M.W. 229·14
Space group: $C2/c$	$Z = 4$
$\lambda(Mo\ K\bar{\alpha}) = 0\cdot7107$ Å	$V = 808\cdot1$ Å³
$a = 12\cdot490$ (2) Å	$D_{obs} = 1\cdot90$ g cm⁻³ (pycnometric)
$b = 6\cdot024$ (1)	$D_{cal} = 1\cdot786$ g cm⁻³
$c = 10\cdot740$ (2)	$F(000) = 452$
$\beta = 90\cdot49$ (1)°	$\mu = 25\cdot386$ cm⁻¹

unobserved as they had an intensity less than their counting standard deviation. The intensities were corrected for Lorentz and polarization effects but no absorption correction was applied. A Wilson plot was calculated and rough values for the scale factor and the overall thermal parameter were obtained. Anomalous dispersion corrections were introduced for cobalt and sulphur atoms with values taken from *International Tables for X-ray Crystallography* (1962).

Solution and refinement of the structure

The Harker sections of a Patterson map revealed the cobalt atom at a centre of symmetry and further Fourier syntheses gave the rest of the non-hydrogen atoms. The parameters of an isotropic model and the corresponding anisotropic one were refined by full-matrix least squares. A difference synthesis revealed all the hydrogens attached to the water molecules. A mixed model, with isotropic values for the hydrogen atoms, was refined using a weighting scheme so as to give a constant average for $w\Delta^2$ ($\Delta = |F_o - F_c|$), when analysed in either $|F_o|$ or $\sin\theta/\lambda$, namely $w = 0\cdot3336/(0\cdot4042 + 0\cdot0128|F_o|)^2$ if $|F_o| < 3\cdot67$ and $w = 0\cdot3336/(-0\cdot3919 + 0\cdot0346|F_o|)^2$ otherwise. Through a parallel calculation the corresponding non-centrosymmetric space group was rejected.

The final values for the indices R, R_w and σ_1 (the e.s.d. for an observation of unit weight) were 0·03, 0·04 and 1·6 respectively, with a maximum shift over error of 0·4 in the last cycle of refinement. Final covariances, in the 0·47–0·67 range, were found between the scale factor and thermal parameters for cobalt and sulphur and between the thermal parameters of these atoms. A final difference synthesis had no significant peaks, the noise being within ±0·38 e Å^{-3}.

The atomic scattering factors for the hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962), while for the rest of the atoms those from Cromer & Waber (1965) were used.

The values of the parameters from the last cycle of least squares, with their e.s.d.'s are given in Table 2.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31464 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
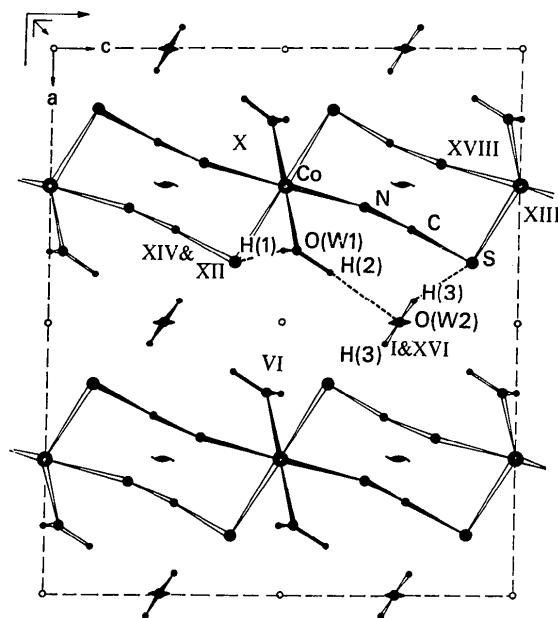

Fig. 1. The structure viewed along the *b* axis.

Results and discussion

The interatomic distances within the structure can be seen in Table 3, the numbering being that given in Fig. 1, which corresponds to a view of the structure along the *b* axis.

Table 3. *Interatomic distances (Å) and angles (°) with the e.s.d.'s given in parentheses*

	Distance		Angle
Co——N	2·064 (2)	N———Co———O(W1)	87·23 (7)
Co———O(W1)	2·091 (2)	N———Co———S^{xiv}	87·84 (5)
Co———S^{xiv}	2·601 (1)	O(W1)-Co———S^{xiv}	88·11 (5)
Co———H(1)	2·63 (5)	O(W1)-Co———H(1)	15 (1)
Co———H(2)	2·66 (4)	O(W1)-Co———H(2)	16 (1)
N———C	1·160 (3)	Co———N———C	165·9 (2)
N———O(W1)	2·866 (2)		
N———O(W1)^x	3·008 (2)		
N———S^{xiv}	3·259 (2)		
N———S^{xviii}	3·381 (2)		
C———S	1·664 (2)	N———C———S	179·2 (2)
		Co———S^{xiv}——C^{xiv}	101·24 (7)
O(W1)-H(1)	0·81 (5)	H(1)——O(W1)-H(2)	106 (4)
O(W1)-H(2)	0·88 (5)	H(2)——O(W1)-Co	122 (3)
O(W1)-S^{xiv}	3·283 (2)	H(1)——O(W1)-Co	124 (3)
O(W1)-S^{xviii}	3·391 (2)		
O(W2)-H(3)	0·87 (6)	H(3)——O(W2)-H(3)^{xvi}	101 (6)

Symmetry code
x	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
xiv	x	$-y$	$z-\frac{1}{2}$
xvi	$1-x$	y	$\frac{1}{2}-z$
xviii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

The cobalt atom is surrounded by six centrosymmetrically related atoms, namely two nitrogens, the oxygens atoms of two water molecules and two sulphur atoms. In this way one can build up a coordination octahedron with all interatomic distances (Table 4) larger than the estimated sum of the covalent radii (Pauling, 1960). The differences are significant in terms of the least-squares e.s.d.'s; the smallest difference corresponds to Co–N, the next to Co–O(W1) and the largest to Co–S^{xiv}. The three dihedral angles defined by the planes Co–N–O(W1), Co–O(W1)-S^{xiv} and Co–N–S^{xiv} are 88·0, 87·3 and 88·2°. On the other hand, these distances are much shorter than the expected van der Waals contacts; consequently it was believed

Table 2. *Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$), given according to the expression* $\exp(-2\pi\sum U_{ij}a_i^* a_j^* h_i h_j)$ *for the heavy atoms, and according to* $\exp(-2\pi^2 U/d_{hkl}^2)$ *for the hydrogen atoms*

The least-squares e.s.d.'s given in parentheses refer to the last digit.

	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2500	2500	5000	284 (2)	240 (2)	159 (2)	−50 (1)	−54 (1)	34 (1)
N	2908 (2)	1190 (3)	6715 (2)	410 (9)	321 (9)	206 (8)	21 (7)	−47 (7)	45 (6)
C	3306 (2)	770 (3)	7666 (2)	306 (8)	239 (8)	202 (8)	2 (6)	−20 (6)	20 (6)
S	3893 (0)	178 (1)	9021 (0)	347 (3)	312 (3)	218 (2)	−27 (2)	−100 (2)	56 (2)
O(W1)	3740 (1)	4787 (3)	5269 (2)	379 (8)	323 (8)	386 (8)	−115 (6)	−113 (6)	51 (6)
O(W2)	5000	−4304 (5)	7500	526 (14)	423 (13)	435 (14)	0	10 (11)	0
H(1)	3728 (33)	6050 (81)	5015 (40)	413 (108)					
H(2)	4116 (34)	4827 (70)	5965 (44)	351 (107)					
H(3)	4550 (48)	−3384 (105)	7836 (62)	785 (194)					

that there is not much covalent character in the cobalt interactions, but a rather ionic one of the type found for other cations (Mokuolu & Speakman, 1975). In this way the cobalt atom is joined to the nitrogen ends of the NCS group (Lindqvist & Strandberg, 1957) in an almost radial form, as the angle Co–N–C is 165·9°, which is in the 150–180° range of reported values; deviations from 180° have been related to steric effects (Drew & Bin Othman, 1975). The cobalt atom also coordinates to another NCS group through the sulphur atom of a nearby molecule, in a weaker and non-radial form, as the angle Co–S^{xiv}–C^{xiv} is 101·2° (Caira & Nassimbeni, 1975). In this way, it seems important to denote the presence of cobalt–cobalt links through bidentate NCS groups.

Table 4. *Estimated values taken for the covalent and van der Waals radii, and distances less than 4 Å from the cobalt atom to all neighbours, with the e.s.d.'s in parentheses*

Covalent radii (Å)		van der Waals radii (Å)	
Co	1·32	Co	2·12
N	0·70	N	1·50
O	0·66	O	1·40
S	1·04	S	1·85

	Distance (Å)		Distance (Å)
Co–N	2·064 (2)	Co–C	3·201 (2)
O(W1)	2·091 (2)	N^x	2·064 (2)
C^x	3·201 (2)	O(W1)^x	2·091 (2)
C^{xiv}	3·350 (2)	S^{xiv}	2·601 (1)
C^{xviii}	3·350 (2)	S^{xviii}	2·601 (1)

The NCS group shows the values which characterize its stability through different types of compounds (Mokuolu & Speakman, 1975). The N–C distance of 1·160 Å can be considered as defining a triple bond, while the C–S distance of 1·664 Å is much shorter than a normal single bond. Accordingly some intermediate character has to be assigned to it (Konnert & Britton, 1971). The NCS group is linear (179·2°), the Co atom being 0·52 Å from the line, due to the Co–N–C angle. On the other hand the group almost lies on the Co–N–O(W1) plane (0·02 and 0·07 Å deviations for C and S). As far as the vibrational parameters of

the group are concerned they are approximately equal for both ends. If the NCS group were not interacting through the sulphur end, one would expect sulphur to have higher thermal parameters than nitrogen.

The O(W1) water molecule makes angles of 20·3° and 76·2° with the planes Co–O(W1)–N and Co–O(W1)–S ^{iv} respectively, in such a way that it is nearly perpendicular (89·1°) to the other water molecule. The oxygen O(W1) of the coordinated water molecule has thermal values comparable with those for the NCS group, while the oxygen O(W2), of the remaining water molecule located on a twofold axis, possesses the highest thermal parameters in the structure.

Table 5 gives the proposed hydrogen bonding scheme which forms the crystalline structure. The three H-bonds are marked with an asterisk. The rest represent contacts with a geometry which is not the expected one for H-bonds (Hamilton, 1968). The two water molecules are linked within the structure in a different manner; one is bonded to the cobalt and has two H-bonds while the other is only linked through H-bonding. In addition the differential thermal analysis of the crystal shows that the water molecules are non-equivalent (Guerrero Laverat, 1976), in support of the different interactions proposed. On the other hand the sulphur atom plays quite an important role since it is not only interacting with the cobalt but also joining the two water molecules through the proposed H-bonds.

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Table 5. *Hydrogen bonds (*)]and short* X–H$\cdots$Y *van der Waals contacts*

Distances are in Å and angles in degrees with the e.s.d.'s in parentheses.

X	H	Y	Distances X$\cdots$Y	H$\cdots$Y	Angles X–H$\cdots$Y	H–X$\cdots$Y
O(W1)	H(1)	S^{xii}*	3·322 (2)	2·52 (5)	172 (4)	6 (3)
O(W1)	H(2)	N	2·866 (2)	2·78 (4)	86 (3)	76 (3)
O(W1)	H(2)	O(W1)^{vi}	3·215 (2)	3·01 (4)	96 (3)	69 (3)
O(W1)	H(2)	O(W2)^{i}*	2·908 (2)	2·05 (5)	167 (4)	9 (3)
O(W2)	H(3)	S*	3·451 (2)	2·63 (6)	158 (5)	17 (4)
O(W2)		O(W1)^{xiii}	3·389 (2)	2·93 (7)	114 (5)	52 (4)

Symmetry code

i	x	$1+y$	z
vi	$1-x$	$1-y$	$1-z$
xii	x	$1-y$	$z-\frac{1}{2}$
xiii	x	$-y$	$\frac{1}{2}+z$

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Structure Cristalline et Moléculaire de la Glycocyamine

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Glycocyamine crystallizes in the monoclinic system $P2_1/c$; $a = 4\cdot937$, $b = 6\cdot004$, $c = 17\cdot519$ Å; $\beta = 101\cdot93°$. The structure was solved by the direct method. Counter data collected with Mo $K\alpha$ radiation were used in the refinement. The final R value is $0\cdot064$ for 1504 observed reflexions. All the hydrogen atoms have been located on difference Fourier maps. The molecular structure corresponds to that of a zwitterion. It can be described as consisting of two groups of atoms lying on two planes which form an angle of $3\cdot99°$. The average value of the three C–N bond lengths in the guanidyl group is $1\cdot327$ Å. The molecules are held together by a network of hydrogen bonds.

Introduction

La glycocyamine (acide guanidino-acétique) est une base guanidique monosubstituée. Sa biosynthèse résulte d'une réaction de transamidination de la glycine par l'arginine. Elle est une étape dans la formation de la créatine (acide *N*-méthylguanidino-acétique) qui n'en diffère que par une deuxième substitution sur l'azote.

Alors que la créatine et l'arginine ont fait l'objet de nombreux travaux cristallographiques (Mendel & Crowfoot-Hodgkin, 1954; Jensen, 1955; Donohue & Metz, 1964; Karle & Karle, 1964; Mazumdar & Srinivasan, 1964; Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970; Hanson, Jensen & Herriott, 1972), la glycocyamine a été peu étudiée (Roy, Mazumdar & Saha, 1967). Nous avons entrepris son étude dans le but d'obtenir des précisions suffisantes sur la conformation de la molécule (et particulièrement sur les paramètres structuraux du groupement guanidique) pour pouvoir la comparer à celles des autres bases guanidiques.

Cette étude entre dans le cadre général du travail que nous avons entrepris depuis 1972 sur les bases guanidiques et leurs dérivés *N*-phosphorylés qui interviennent dans les processus biochimiques des mammifères et des invertébrés marins.

Détermination de la structure

Les cristaux de glycocyamine, dont la formule chimique est:

$$H_2N\!\!>\!\!\!C\text{–NH–}CH_2\text{–}C\!\!<^O_{OH}$$
$$HN$$
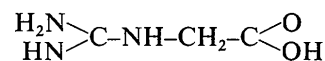
ont la forme de parallélépipèdes transparents. Les dimensions maximales du cristal utilisé sont $0,25 \times 0,3 \times 0,5$ mm. Les dimensions de la maille monoclinique ont été déterminées par une méthode de moindres carrés en utilisant 25 réflexions de grand angle de Bragg mesurées au diffractomètre automatique: $a = 4,937 \pm 0,002$, $b = 6,004 \pm 0,002$, $c = 17,519 \pm 0,004$ Å; $\beta = 101,93° \pm 0,01°$; $P2_1/c$; $Z = 4$; $D_c = 1,545$, $D_m = 1,54$ g cm^{-3}.

Les mesures d'intensité ont été effectuées à l'aide d'un diffractomètre automatique Philips PW 1100. 1506 réflexions indépendantes ont été mesurées en utilisant le rayonnement $K\alpha$ du molybdène. Les corrections de Lorentz et de polarisation ont été appliquées aux intensités mesurées mais les erreurs dues à l'absorption ont été négligées ($\mu = 1,40$ cm^{-1}; $\mu r = 0,05$).

La structure a été trouvée sans difficulté à l'aide du programme *MULTAN* qui a fourni les positions des 8 atomes de la molécule. Mais, étant donné la difficulté