# Crystal Structure of *trans*-Sulphiteisothiocyanatebisethylenediaminecobalt(III) Dihydrate

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IT is assumed that the $SO_3^{2-}$ ligand has a *trans*-labilizing effect in octahedral $Co^{III}$ complexes,[1] but there is no direct evidence of a structural *trans*-effect. From the interpretation of the i.r. spectra it was inferred that in a number of $Co^{III}$ sulphite complexes the sulphito-group is co-ordinated through the sulphur atom, and that the S–O bonds of the ligand are strengthened on co-ordination,[2] but no *X*-ray structural work on these complexes has been reported so far.

We have determined the crystal structure of one of these complexes, $Co(en)_2\,SO_3NCS,2H_2O$. Crystal data: $C_5H_{12}O_5N_5S_2Co$, $M = 353{\cdot}25$, monoclinic, $a = 9{\cdot}06$, $b = 6{\cdot}59$, $c = 22{\cdot}84$ Å, $\beta = 95{\cdot}4°$, $U = 1357{\cdot}5$ Å$^3$, $D_m = 1{\cdot}71$ (by flotation), $Z = 4$, $D_c = 1{\cdot}73$, space group $P2_1/c$ ($C_{2h}^5$, No. 14), $\mu = 18{\cdot}5$ cm.$^{-1}$ for Mo-$K$ radiation.

Initial co-ordinates for the cobalt and sulphur atoms were obtained from a three-dimensional Patterson synthesis, all the light atoms other than

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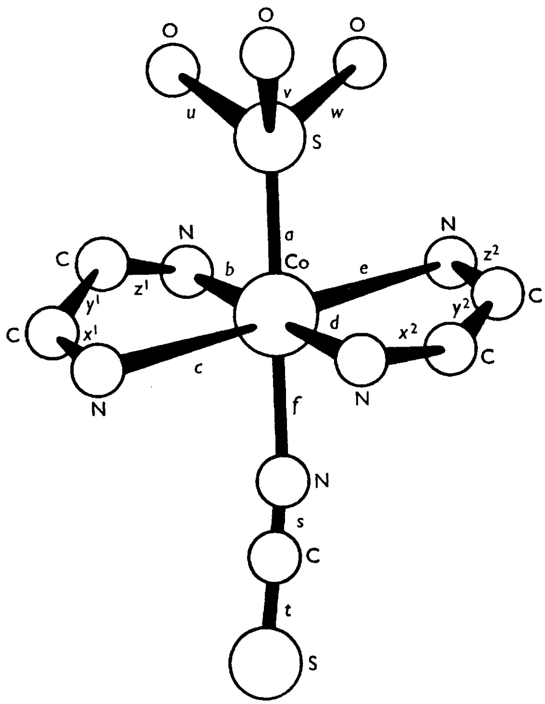

$a$ = 2·202 (5) Å
$b$ = 1·948 (15)
$c$ = 1·939 (20)
$d$ = 1·925 (15)
$e$ = 1·964 (15)
$f$ = 1·975 (15)

$ab$ = 91·6 (0·5)°
$ac$ = 89·2 (0·5)
$ad$ = 90·3 (0·5)
$ae$ = 92·6 (0·5)
$af$ = 177·2 (0·5)
$bc$ = 87·0 (0·7)
$de$ = 87·8 (0·8)

$x^1$ = 1·49 (3) Å
$z^1$ = 1·50 (3)
$y^1$ = 1·55 (3)
$x^1y^1$ = 107·8 (2·0)°
$y^1z^1$ = 104·4 (2·0)
$x^1c$ = 109·8 (1·0)
$z^1b$ = 108·0 (1·0)

$x^2$ = 1·49 (3) Å
$z^2$ = 1·49 (3)
$y^2$ = 1·36 (3)
$x^2y^2$ = 113·6 (2·0)°
$y^2z^2$ = 110·0 (2·0)
$x^2d$ = 111·3 (1·5)
$z^2e$ = 107·0 (1·0)

$u$ = 1·450 (15) Å
$v$ = 1·476 (15)
$w$ = 1·457 (15)

$uv$ = 114·0 (1·1)°
$uw$ = 109·2 (1·1)
$vw$ = 111·1 (1·1)

$au$ = 108·2 (0·5)°
$av$ = 107·8 (0·5)
$aw$ = 109·2 (0·5)

$s$ = 1·173 (25) Å
$t$ = 1·628 (15)

$ts$ = 178·4 (1·5)°
$ts$ = 168·1 (1·5)

FIGURE. *Structure of the complex in* $Co(en)_2SO_3NCS,2H_2O$. *Standard deviations, givien in parentheses, are in units of the last decimal place.*

hydrogen were located by three dimensional Fourier and difference synthesis. Full-matrix least-squares refinement with individual isotropic temperature factors for each atom (hydrogen atoms not included), gave a discrepancy index $R_1$ of 10·7% for 1146 independent non-zero reflexions, measured with microdensitometer on mechanically integrated equi-inclination Weissenberg and precession photographs taken with Mo-$K_\alpha$ radiation. The stereochemistry of the complex, together with the interatomic distances and angles, is depicted in the Figure. The primary ligand atoms are arranged in approximate octahedral geometry about the metal atom, as is usual in $Co^{III}$ complexes. A least-squares calculation of the best plane for cobalt and the four nitrogen atoms of the ethylenediamine groups shows that the maximum deviation from the plane is of less than 0·02 Å. The dimensions and Co–N–C angle of the isothiocyanate group is similar to that found in other isothiocyanate compounds.[3] One of the ethylenediamine groups has odd dimensions, and does not adopt the usual *gauche*-configuration. Since the temperature factors of the carbon atoms of this group are rather high, 5·8 and 6·7 Å², disorder might be the explanation of the anomalies. The water molecules are distributed in pairs, the O · · · O distance within each pair is 2·85 Å, close enough to be involved in hydrogen bonding. One of the oxygen atoms of each sulphito-group is also sufficiently close to the oxygen atom of a water molecule to be involved in hydrogen bonding, O · · · O ($SO_3$) = 2·87 Å. It seems worthwhile to point out the following features:

(1) The Co–N (NCS) distance (1·97 Å) is practically the same as the Co–N (en) distances (mean $1{\cdot}94_5$), there being no evidence of a significant structural *trans*-effect within the accuracy of our data. All the Co–N distances are similar to those found in a number of other $Co^{III}$ complexes.[4]

(2) The sulphito-group is co-ordinated through the sulphur atom to the metal, and the Co–S distance (2·202 Å) is somewhat shorter than the sum of Pauling's covalent radii (2·26 Å), indicating that this bond might have some $\pi$-character.

(3) The co-ordinated sulphito-groups have shorter S–O distances (average $1{\cdot}46_3$ Å), and the mean O–S–O angle (111°) is larger, than the corresponding one in the free ion [1·53 Å and 105° in $(NH_4)_2SO_3,H_2O$].[5] The mean of the nonbonded O · · · O distances is 2·41 Å, this value corresponds to a tetrahedral distortion, as represented on a plot of nonbonded O · · · O against S–O distances, similar to that found in a number of sulphates.[6] The features described in this paragraph are also observed in the geometry of the sulphito-group in $Pd(NH_3)_3SO_3$.[7]

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