

## The Crystal Structure of $(-)$ <sub>589</sub>-Dinitrobis(ethylenediamine)cobalt(III) $(-)$ <sub>589</sub>-Dinitrooxalatodiammincobaltate(III) Monohydrate

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$(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>] $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>] crystallizes in the orthorhombic space group  $P2_12_12_1$  with  $a = 12.643$  (2),  $b = 24.948$  (2),  $c = 6.594$  (1) Å and  $Z = 4$ . The structure was determined by the heavy-atom method and refined by least-squares calculations to  $R = 0.041$  for 2809 observed amplitudes. The complex anion is a *cis-cis* isomer: a Co atom is surrounded nearly octahedrally by two N atoms of the nitro groups, two N atoms of the ammonia molecules, both in *cis* positions, and two O atoms of an oxalato group. The absolute configuration of the complex anion,  $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> can be designated as *A*, providing that the chirality is defined by the line joining the two N atoms of the nitro groups and that joining the two N atoms of the ammonia groups. In the two chelate rings of [Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> the C atoms exhibit much greater thermal motion perpendicular to the plane formed by the two N atoms and the Co atom.

### Introduction

Three isomers of dinitrooxalatodiammincobaltate(III) complexes were isolated and the optically active *cis-cis* isomers resolved (Ito & Shibata, 1975). The complex anion  $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> has only one chelate ring and the optical activity arises from the dissymmetric arrangement of four monodentates. The absolute configuration of the complex anion is of particular importance, since no empirical relation between the circular dichroism spectra and the absolute configuration of such complexes has been established. The crystals of the title compound were subjected to crystal structure analysis to establish the absolute configuration and the conformational details.

### Experimental

Crystals of  $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>] $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>].H<sub>2</sub>O were kindly supplied by Professor M. Shibata of Kanazawa University. They are orange red needles. The density was measured by flotation in CH<sub>2</sub>I<sub>2</sub>/CCl<sub>4</sub>. Approximate cell dimensions were determined by oscillation and Weissenberg photographs, the final cell dimensions being measured on a Rigaku four-circle computer-controlled diffractometer with graphite-monochromated Mo *K*α radiation and a scintillation counter. Intensities were measured for a crystal of dimensions 0.20 × 0.20 × 0.31 mm, the  $\omega$ -2 $\theta$  scan technique being employed. Of 3312 reflexions scanned within the range  $2\theta \leq 60^\circ$ , 2809 with  $|F| \geq 3\sigma$  were considered to be observed and were used for structure analysis. In converting intensities to structure factors, Lorentz and polarization factors appropriate to monochromated radiation were used. An absorption correction was not applied.

### Crystal data

$(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>] $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(NH<sub>3</sub>)<sub>2</sub>].H<sub>2</sub>O,  $M = 562.2$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.643$  (2),  $b = 24.948$  (2),  $c = 6.594$  (1) Å,  $U = 1996.7$  Å<sup>3</sup>,  $D_m = 1.85$ ,  $D_x = 1.87$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo } K\alpha, \lambda = 0.7107 \text{ \AA}) = 15.8$  cm<sup>-1</sup>.

### Structure determination and refinement

The structure was solved by Patterson and Fourier techniques. Block-matrix least-squares refinement converged to  $R = 0.14$  with isotropic temperature factors and 0.041 when anisotropic vibration was permitted for all atoms except H. Unit weight was given to all reflexions. The atomic scattering factors for Co, N, C and O as well as the corrections for anomalous scattering of Co were taken from *International Tables for X-ray Crystallography* (1962). For H the values given by Stewart, Davidson & Simpson (1965) were used. The final atomic parameters are listed in Table 1.\*

### Determination of the absolute configuration

The absolute structure was determined with reference to the known absolute configuration of the complex cation  $(-)$ <sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> (Matsumoto & Kuroya, 1972). To check this result the observed and calculated intensity ratios of the six Bijvoet pairs are compared in Table 2, for which the observed  $|F(hkl)|$  and  $|F(\bar{h}\bar{k}\bar{l})|$

\* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31349 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

differed by more than 12%. The agreement in the observed and calculated intensity ratios clearly confirms the absolute configuration determined by the use of an internal reference centre. The absolute configuration of the complex anion  $(-)_589\text{-}[\text{Co}(\text{NO}_2)_2(\text{ox})(\text{NH}_3)_2]$  is illustrated in Fig. 1.

### Description and discussion of the structure

The crystal is essentially ionic, comprising the complex ions  $[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$  and  $[\text{Co}(\text{NO}_2)_2(\text{ox})(\text{NH}_3)_2]^-$ , and water molecules. A projection of the structure along *c* is shown in Fig. 2, together with the numbering of the atoms. In the complex anion the Co atom is surrounded nearly octahedrally by two O atoms of an oxalato group and four N atoms, of which two belong to the nitro groups and the remaining two are from ammonia molecules. The two nitro groups and the two ammonia molecules are in *cis* positions. The geometry of the oxalato and nitro groups is much the same as that observed in related complexes (*e.g.* Oonishi, Sato & Saito, 1974). Other bond distances and angles are all normal, as shown in Table 3.

The shape and the size of the complex cation  $[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$  is similar to those described by Matsumoto & Kuroya (1972) and will not be discussed further. One remarkable feature is that the C atoms of the Co-en ring exhibit larger thermal motion perpendicular to the plane of the chelate ring, as shown in Fig. 3. The C(1)–C(2) and C(3)–C(4) distances are unusually shorter than the normal C–C single bond. The shortening seems to be due to errors introduced by the correlation of the positional parameters with the thermal motion of the C atoms. Similar anisotropic vibration of C atoms in a Me-en ring was also observed for  $[\text{Co}(\text{en})_3]^{3+}$  (Iwata, Nakatsu & Saito, 1969),  $[\text{Co}(\text{en})_2\text{SO}_3\text{NCS}]$  (Baggio & Becka, 1969) and  $[\text{Cu}(\text{en})_2\text{H}_2\text{O}]^{2+}$  (Williams, Larson & Cromer, 1972).

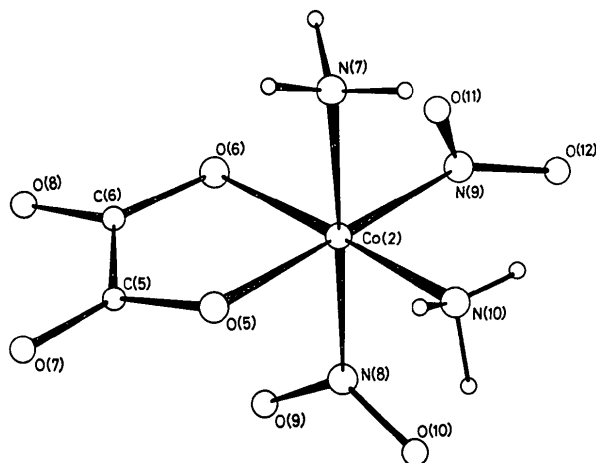


Fig. 1. The absolute configuration of the anion.

The packing of the complex cations and anions is illustrated in projection down *c* in Fig. 2. Interatomic distances are listed in Table 4. The complex cations, anions and the water molecules are involved in a complicated three-dimensional network of hydrogen bonds, which is indicated by broken lines in Fig. 2. O(7) of an oxalato group is bonded to the two amino

Table 1. Positional and thermal parameters

(a) Final positional parameters and their estimated standard deviations (in parentheses)

The values have been multiplied by  $10^4$  for the non-hydrogen atoms and by  $10^3$  for the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
Co(1)	5443 (1)	4506 (0)	1557 (1)
Co(2)	5967 (1)	2060 (0)	4467 (1)
N(1)	4456 (3)	3866 (2)	1783 (7)
N(2)	4350 (4)	4837 (2)	-130 (7)
N(3)	6332 (4)	5154 (2)	1273 (8)
N(4)	6524 (4)	4126 (2)	3149 (7)
N(5)	4859 (4)	4824 (2)	4001 (7)
N(6)	6147 (4)	4169 (2)	-794 (7)
N(7)	4590 (4)	1809 (2)	3498 (10)
N(8)	7305 (4)	2314 (2)	5451 (10)
N(9)	6393 (4)	1312 (2)	4843 (9)
N(10)	6498 (4)	2051 (2)	1741 (8)
C(1)	3475 (5)	3996 (3)	806 (17)
C(2)	3476 (6)	4447 (3)	-518 (15)
C(3)	7252 (7)	3819 (5)	1848 (14)
C(4)	7012 (7)	3801 (4)	-141 (13)
C(5)	5248 (4)	3036 (2)	5851 (8)
C(6)	5142 (5)	2618 (2)	7604 (9)
O(1)	6063 (5)	5532 (2)	164 (12)
O(2)	7172 (5)	5186 (3)	1986 (12)
O(3)	3975 (5)	4966 (4)	4147 (10)
O(4)	5404 (5)	4886 (2)	5502 (7)
O(5)	5541 (3)	2826 (1)	4176 (5)
O(6)	5375 (3)	2116 (1)	7112 (6)
O(7)	5054 (4)	3541 (1)	6122 (6)
O(8)	4896 (4)	2775 (2)	9314 (7)
O(9)	7393 (5)	2535 (4)	7056 (11)
O(10)	8056 (4)	2314 (4)	4455 (15)
O(11)	6259 (6)	1071 (2)	6363 (11)
O(12)	6757 (10)	1038 (3)	3600 (14)
O(13)	4780 (6)	1222 (2)	-294 (10)
H(N1)	430 (5)	376 (2)	301 (10)
H'(N1)	481 (4)	352 (2)	135 (8)
H(N2)	467 (5)	489 (3)	-138 (10)
H'(N2)	414 (5)	517 (3)	45 (12)
H(N4)	626 (5)	390 (2)	387 (10)
H'(N4)	691 (5)	440 (3)	382 (10)
H(N6)	640 (5)	448 (2)	-146 (10)
H'(N6)	573 (5)	404 (2)	-165 (10)
H(Cl)	305 (7)	416 (3)	175 (14)
H'(Cl)	301 (5)	365 (3)	41 (11)
H(C2)	360 (6)	432 (3)	-151 (14)
H'(C2)	282 (6)	464 (3)	-28 (13)
H(C3)	762 (5)	357 (3)	242 (11)
H'(C3)	789 (6)	422 (3)	158 (13)
H(C4)	759 (5)	378 (3)	-114 (12)
H'(C4)	662 (6)	335 (3)	35 (14)
H(N7)	405 (5)	210 (3)	323 (12)
H'(N7)	418 (6)	159 (3)	433 (13)
H''(N7)	476 (5)	164 (2)	226 (10)
H(N10)	613 (5)	228 (2)	116 (10)
H'(N10)	661 (6)	174 (3)	138 (14)
H''(N10)	719 (6)	223 (3)	170 (13)
H(O13)	566 (4)	116 (2)	6 (9)
H'(O13)	475 (7)	76 (3)	-90 (14)

Table 1 (cont.)

(b) Final thermal parameters and their estimated standard deviations (in parentheses). The  $U_{ij}$ 's are defined by:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-3}]$ . The isotropic temperature factor is defined by  $\exp[-8\pi^2U(\sin \theta/\lambda)^2]$ . Mean value of  $U$  for the hydrogen atoms is 0.09 (2) Å<sup>2</sup>.

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co(1)	33 (0)	27 (0)	27 (0)	5 (0)	1 (0)	-2 (0)
Co(2)	31 (0)	29 (0)	42 (0)	-4 (0)	1 (0)	-3 (0)
N(1)	38 (2)	30 (2)	38 (2)	6 (2)	-5 (2)	-2 (2)
N(2)	49 (3)	35 (2)	45 (3)	2 (2)	8 (2)	21 (2)
N(3)	49 (3)	37 (2)	52 (3)	15 (2)	-2 (2)	-4 (2)
N(4)	42 (2)	52 (3)	38 (2)	8 (2)	7 (2)	4 (2)
N(5)	50 (3)	44 (2)	43 (3)	4 (2)	-3 (2)	-12 (2)
N(6)	43 (2)	45 (2)	34 (2)	8 (2)	-5 (2)	-8 (2)
N(7)	38 (2)	56 (3)	86 (4)	-4 (2)	2 (3)	-26 (3)
N(8)	40 (3)	69 (3)	71 (4)	2 (2)	7 (3)	-13 (3)
N(9)	62 (3)	37 (2)	65 (4)	-16 (2)	-5 (3)	3 (2)
N(10)	65 (3)	46 (3)	51 (3)	-15 (3)	-9 (3)	-6 (3)
C(1)	48 (4)	71 (4)	146 (9)	27 (3)	35 (5)	40 (6)
C(2)	68 (4)	66 (4)	121 (7)	21 (4)	52 (5)	22 (5)
C(3)	93 (6)	190 (11)	66 (6)	-97 (7)	0 (5)	-2 (7)
C(4)	104 (7)	151 (8)	66 (5)	-88 (7)	13 (5)	-34 (6)
C(5)	39 (2)	30 (2)	35 (2)	1 (2)	3 (2)	-2 (2)
C(6)	55 (3)	34 (3)	39 (3)	-2 (2)	1 (3)	1 (2)
O(1)	95 (4)	54 (3)	186 (7)	31 (3)	21 (5)	47 (4)
O(2)	99 (5)	107 (5)	165 (7)	73 (4)	65 (5)	55 (5)
O(3)	71 (4)	225 (8)	94 (5)	-52 (5)	16 (4)	-89 (6)
O(4)	105 (4)	97 (4)	39 (2)	-12 (4)	7 (3)	-22 (3)
O(5)	56 (2)	31 (2)	32 (2)	-5 (2)	-1 (2)	2 (1)
O(6)	64 (2)	31 (2)	48 (2)	-6 (2)	-10 (2)	4 (2)
O(7)	73 (3)	28 (2)	42 (2)	-6 (2)	3 (2)	-6 (2)
O(8)	122 (4)	48 (2)	37 (2)	-13 (3)	-6 (3)	2 (2)
O(9)	93 (5)	240 (9)	91 (5)	77 (6)	12 (4)	-43 (6)
O(10)	35 (3)	342 (12)	188 (9)	38 (5)	-25 (5)	-140 (9)
O(11)	157 (6)	50 (3)	125 (6)	-28 (4)	-25 (6)	23 (4)
O(12)	449 (17)	104 (5)	147 (7)	-173 (8)	-146 (10)	44 (6)
O(13)	155 (6)	60 (3)	82 (4)	16 (4)	-22 (5)	-7 (3)

Table 2. Determination of the absolute configuration

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	$ F_c $	$ F_o(hkl) / F_o(\bar{h}k\bar{l}) $	$ F_c(hkl) / F_c(\bar{h}k\bar{l}) $
4	3	1	22.7	24.3	1.31	1.25
4	3	1	17.3	19.4		
3	4	1	18.2	17.6	1.14	1.18
3	4	1	16.0	14.9		
1	5	1	7.8	8.3	0.64	0.64
1	5	1	12.1	13.0		
2	8	1	32.8	32.4	0.88	0.89
2	8	1	37.1	36.5		
1	10	1	36.6	37.5	1.12	1.12
1	10	1	32.6	33.5		
1	6	2	53.3	53.4	1.16	1.15
1	6	2	45.8	46.3		

N atoms, N(1) and N(4), of the adjacent complex cation. O(2) of a nitro group is linked to an amino N atom, N(6). N(7) of an ammonia molecule is hydrogen bonded to the water O atom O(13) at a distance of 2.878 Å. O(13) is also bonded to O(11) of an adjacent complex anion shifted by a unit translation along *c*.

An aqueous solution of K(-)<sub>589</sub>-[Co(NO<sub>2</sub>)<sub>2</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>] gives two c.d. peaks at 19500 ( $\Delta\epsilon = -0.89$ ) and at 22300 cm<sup>-1</sup> (+1.47) in the region of the first absorption band (Ito & Shibata, 1975). The optical activity of this complex anion arises from the dissymmetric arrangement of the four monodentates: two nitro

Table 3. Interatomic distances (Å) and bond angles (°) in the complex ions

Complex cation		Complex anion	
Co(1)-N(2)	1.982 (5)	Co(2)-N(7)	1.949 (7)
Co(1)-N(2)	1.943 (5)	Co(2)-N(8)	1.911 (7)
Co(1)-N(3)	1.925 (5)	Co(2)-N(9)	1.890 (6)
Co(1)-N(4)	1.949 (5)	Co(2)-N(10)	1.919 (6)
Co(1)-N(5)	1.929 (5)	Co(2)-O(5)	1.920 (4)
Co(1)-N(6)	1.961 (5)	Co(2)-O(6)	1.903 (4)
N(1)-C(1)	1.432 (12)	O(5)-C(5)	1.269 (7)
N(2)-C(2)	1.469 (11)	O(6)-C(6)	1.280 (7)
N(4)-C(3)	1.456 (13)	C(5)-C(6)	1.535 (8)
N(6)-C(4)	1.470 (11)	C(5)-O(7)	1.246 (7)
C(1)-C(2)	1.389 (15)	C(6)-O(8)	1.228 (8)
C(3)-C(4)	1.347 (16)	N(8)-O(9)	1.189 (11)
N(3)-O(1)	1.213 (10)	N(8)-O(10)	1.155 (13)
N(3)-O(2)	1.165 (10)	N(9)-O(11)	1.169 (10)
N(5)-O(3)	1.172 (10)	N(9)-O(12)	1.145 (14)
N(5)-O(4)	1.216 (8)		
N(1)-Co(1)-N(2)	84.9 (2)	O(5)-Co(2)-O(6)	85.1 (2)
Co(1)-N(1)-C(1)	110.1 (5)	Co(2)-O(5)-C(5)	111.9 (3)
Co(1)-N(2)-C(2)	112.1 (5)	Co(2)-O(6)-C(6)	112.8 (4)
N(1)-C(1)-C(2)	116.8 (9)	O(5)-C(5)-C(6)	115.0 (5)
N(2)-C(2)-C(1)	112.7 (8)	O(6)-C(6)-C(5)	113.7 (5)
N(4)-Co(1)-N(6)	85.1 (2)	O(9)-N(8)-O(10)	115.4 (9)
Co(1)-N(4)-C(3)	111.2 (5)	O(11)-N(9)-O(12)	113.0 (9)
Co(1)-N(6)-C(4)	110.7 (5)	O(5)-C(5)-O(7)	124.6 (5)
N(4)-C(3)-C(4)	116.6 (10)	C(6)-C(5)-O(7)	120.5 (5)
N(6)-C(4)-C(3)	115.7 (9)	O(6)-C(6)-O(8)	125.3 (6)
O(1)-N(3)-O(2)	116.6 (7)	C(5)-C(6)-O(8)	120.9 (6)
O(3)-N(5)-O(4)	116.0 (6)		

groups and two ammonia groups. The absolute configuration of the complex ion can be designated as skew pairs *A*, providing that the chirality is defined by the line joining the two N atoms of the nitro groups

and that joining the two N atoms of the ammonia groups.

The authors are grateful to Professor M. Shibata of Kanazawa University for supplying the specimens. All

Table 4. Relevant interatomic distances less than 3.4 Å outside the complex ions with their standard deviations in parentheses

Key to symmetry operations

(i)	$x$	$y$	$z$
(ii)	$0.5-x$	$-y$	$0.5+z$
(iii)	$0.5+x$	$0.5-y$	$-z$
(iv)	$x$	$y$	$1.0+z$
(v)	$-x$	$0.5+y$	$-0.5-z$

N(1)····O(5 <sup>i</sup> )	3.251 (5)	N(6)····O(4 <sup>iv</sup> )	3.130 (7)
N(1)····O(7 <sup>i</sup> )	3.060 (6)*	N(6)····O(7 <sup>iv</sup> )	2.883 (6)*
N(4)····O(7 <sup>i</sup> )	3.043 (6)*	N(10)····O(6 <sup>iv</sup> )	3.370 (7)
N(5)····O(7 <sup>i</sup> )	3.385 (6)	N(10)····O(8 <sup>iv</sup> )	3.110 (7)
N(7)····O(13 <sup>i</sup> )	2.878 (9)*	O(5)····O(8 <sup>iv</sup> )	3.310 (6)
N(10)····O(13 <sup>i</sup> )	3.234 (8)	O(13)····O(6 <sup>iv</sup> )	2.841 (7)
N(6)····O(2 <sup>ii</sup> )	3.007 (8)*	O(13)····O(11 <sup>iv</sup> )	2.914 (10)*
C(4)····O(2 <sup>ii</sup> )	3.246 (12)	N(7)····O(1 <sup>v</sup> )	3.286 (7)
O(2)····O(4 <sup>ii</sup> )	3.221 (9)	O(11)····N(2 <sup>v</sup> )	3.160 (7)*
C(3)····O(13 <sup>iii</sup> )	3.358 (12)	O(11)····O(1 <sup>v</sup> )	3.361 (9)
O(12)····C(2 <sup>iii</sup> )	3.194 (14)	O(12)····N(2 <sup>v</sup> )	3.355 (10)
N(1)····O(8 <sup>iv</sup> )	3.128 (6)*	O(12)····O(3 <sup>v</sup> )	3.277 (11)
N(2)····O(4 <sup>iv</sup> )	3.176 (7)	O(13)····O(4 <sup>v</sup> )	3.211 (7)*

\* Hydrogen bonding.

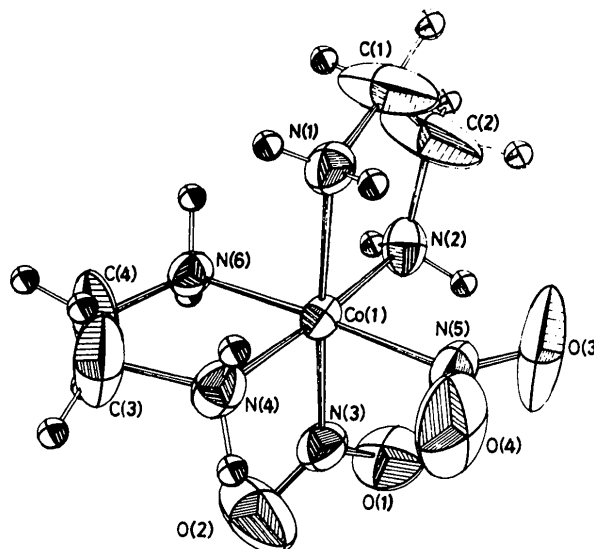


Fig. 3. The thermal ellipsoids of the cation.

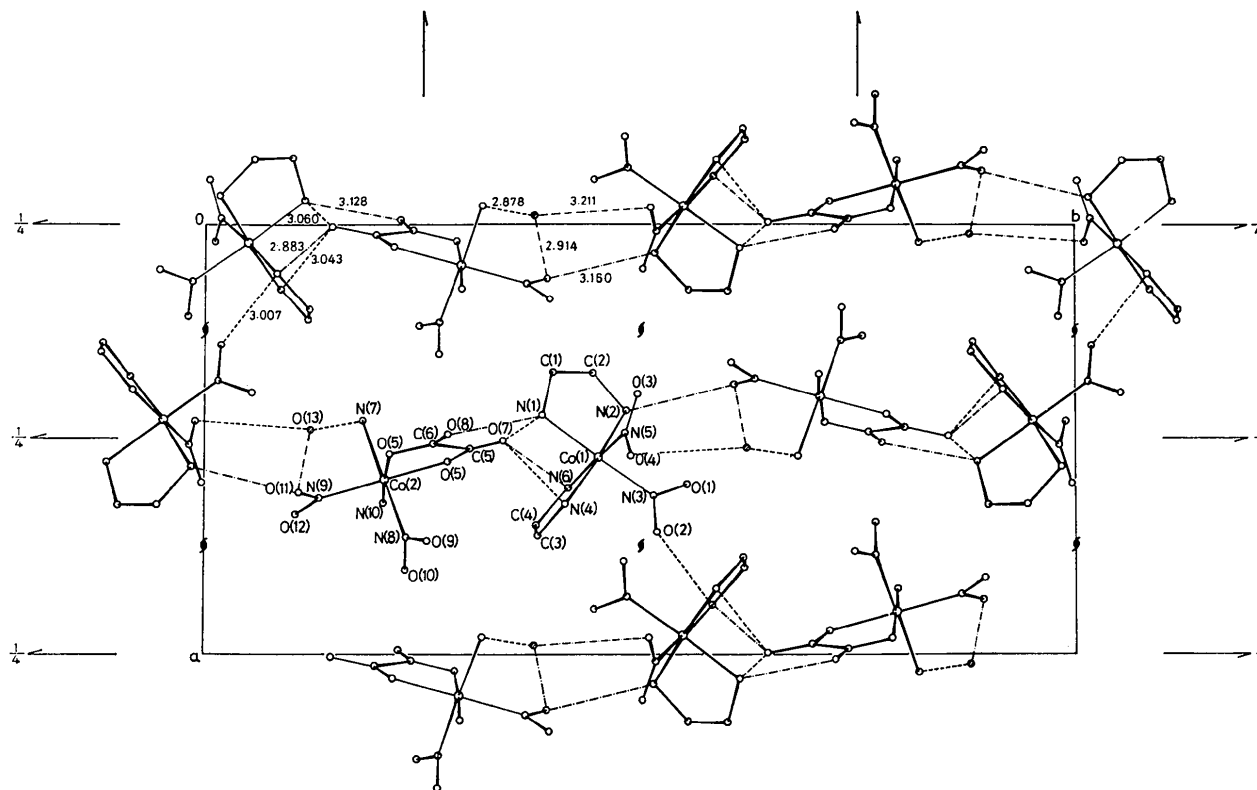


Fig. 2. The crystal structure viewed along *c*. The hydrogen bonds are shown by broken lines. The chained line indicates that an atom at one end displaced by a unit translation along *c* is hydrogen bonded to the atom at the other end.

the computations were carried out on the FACOM 270-30 computer at this Institute. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

### References

- BAGGIO, S. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 946-954.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- ITO, T. & SHIBATA, M. (1975). *Chem. Lett. (Japan)*, pp. 375-378.  
 IWATA, M., NAKATSU, K. & SAITO, Y. (1969). *Acta Cryst.* **B25**, 2562-2571.  
 MATSUMOTO, K. & KUROYA, H. (1972). *Bull. Chem. Soc. Japan*, **45**, 1755-1759.  
 OONISHI, I., SATO, S. & SAITO, Y. (1974). *Acta Cryst.* **B30**, 2256-2258.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.  
 WILLIAMS, R. J., LARSON, A. C. & CROMER, D. T. (1972). *Acta Cryst.* **B28**, 858-864.

*Acta Cryst.* (1976). **B32**, 1188

## Die Kristallstruktur von L.T.-GeS<sub>2</sub>

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The structure of L.T.-GeS<sub>2</sub> has been redetermined. In contrast to an earlier determination it was found that the low-temperature modification of GeS<sub>2</sub> crystallizes in the monoclinic space group *Pc* with cell constants  $a = 6.875$  (5),  $b = 22.55$  (1),  $c = 6.809$  (5) Å and  $\beta = 120.45$  (5)°. The framework of distorted tetrahedra originally described was established in principle. The Ge-S distances are within the limits of 2.17 to 2.29 Å, being in agreement with the values of the other modifications. The final *R* value is 5.4%.

### Einführung

Vom GeS<sub>2</sub> sind bisher drei Modifikationen beschrieben. Neben der Hochdruck-Hochtemperatur-Modifikation (Prewitt & Young, 1965) und der Hochtemperatur-Modifikation (Dittmar & Schäfer, 1975) wurde schon frühzeitig eine dritte nadelförmige Modifikation aufgefunden (Johnson & Wheatley, 1934), deren Struktur von Zachariasen untersucht wurde (Zachariasen, 1936). Die Kristalle wurden als pseudo-hexagonale orthorhombische Säulen in der Raumgruppe *Fdd2* beschrieben. Aus Oszillationsaufnahmen um die Prismenachse von Einkristallen wurden eine Anzahl von Reflexintensitäten abgeschätzt und mit trial-and-error-Verfahren ein bisher nicht wieder aufgefundener Strukturtyp eines Raumnetzverbandes aus GeS<sub>4</sub>-Tetraedern abgeleitet. 1963 wurde jedoch für die gleiche Substanz auf Grund von Pulveraufnahmen ein deformierter CdJ<sub>2</sub>-Typ vorgeschlagen (Ch'ün Hua, Pashinkin & Novoselova, 1963). Demnach hätten die Ge-Atome eine oktaedrische Umgebung. Nachdem aber bereits bei zwei Modifikationen tetraedrische Konfiguration gefunden wurde, erschien dieser Vorschlag nicht sehr wahrscheinlich. Andererseits beruht der Strukturvorschlag von Zachariasen auf, in Betracht der grossen Elementarzelle, verhältnismässig

wenigen Reflexen und enthält dazu einen extrem kurzen Ge-S-Abstand von 2,03 Å. Eine Neubestimmung der Struktur erschien daher notwendig.

### Experimentelles

Es wurden Einkristalle von GeS<sub>2</sub> nach der von Johnson & Wheatley beschriebenen Methode im H<sub>2</sub>S-Strom bei 800°C dargestellt. Dabei wurden schlanke, pseudo-hexagonale Prismen erhalten, die milchig weiss und sehr spröde waren. Weissenberg- (Cu K $\alpha$ , Ni-Filter) und Präzessions-Aufnahmen (Mo K $\alpha$ , Zr-Filter) ergaben ein reziprokes Gitter, das nur eine Gleitspiegelebene (*h0l*-Reflexe nur vorhanden für  $l = 2n$ ) zeigte. Somit sind nur die beiden Raumgruppen *P2/c* und *Pc* möglich. Die anderen von Zachariasen beschriebenen Symmetrie-Elemente der Raumgruppe *Fdd2* waren nur annäherungsweise erfüllt. Hierdurch wurde eine andere Aufstellung der Elementarzelle notwendig. In der Tabelle 1 sind die kristallographischen Daten der alten und neuen Aufstellung einander gegenübergestellt. Der Zusammenhang zwischen beiden Achsen-systemen ist in der Fig. 1 dargestellt. Die ausgebildeten Kristallflächen haben danach die Millerschen Indizes (100), (001), ( $\bar{1}00$ ), (00 $\bar{1}$ ), (10 $\bar{1}$ ) und ( $\bar{1}01$ ). Kopfflächen waren an den Kristallen nicht ausgebildet.