

## The Crystal Structure of (+)<sub>D</sub>-Tris(ethylenediamine)cobalt(III) Chloride Monohydrate, (+)<sub>D</sub>-[Co(en)<sub>3</sub>]Cl<sub>3</sub>.H<sub>2</sub>O

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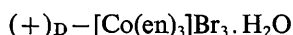
Crystals of (+)<sub>D</sub>-[Co(en)<sub>3</sub>]Cl<sub>3</sub>.H<sub>2</sub>O are tetragonal with space group  $P4_32_12$ . The lattice constants are  $a=9.682$ ,  $c=16.287$  Å, with four formula units in the unit cell. The crystal structure was determined and refined from three-dimensional visual data; refinement was carried out by the method of least-squares. Co, Cl, C, N and O atoms were refined anisotropically and the H atoms isotropically. The final  $R$  index is 0.090. The complex ion has virtual symmetry  $D_3$ . Six nitrogen atoms of the three ligands are bonded nearly octahedrally to the central cobalt atom with an average Co-N distance of  $1.978 \pm 0.004$  Å; the average N-Co-N angle is  $85.3 \pm 0.3^\circ$ . The carbon atoms of the chelate ring show thermal anisotropy best described as an oscillatory motion perpendicular to the C-C bond, similar to the ring puckering motion observed for the same ions in solution.

### Introduction

The crystal structures of [Co(en)<sub>3</sub>]Cl<sub>3</sub>.3H<sub>2</sub>O (Nakatsu, Saito & Kuroya, 1956),



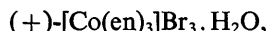
(Nakatsu, Shiro, Saito & Kuroya, 1957), and



(Nakatsu, 1962) have been determined. However, no three-dimensional analysis of a complex salt containing the [Co(en)<sub>3</sub>]<sup>3+</sup> ion has yet been reported, though this complex ion is one of the most familiar and fundamental complex ions in coordination chemistry. An accurate geometry of the complex ion is necessary to construct a theoretical model for the calculation of optical activity, such as rotary strength, *etc.* The structure determination of (+)<sub>D</sub>-tris(ethylenediamine)-cobalt(III) chloride monohydrate was undertaken mainly to obtain structural details of the complex ion, [Co(en)<sub>3</sub>]<sup>3+</sup>.

### Experimental

(+)<sub>D</sub>-[Co(en)<sub>3</sub>]Br<sub>3</sub>.H<sub>2</sub>O was prepared as described by Werner (1912) and was converted into the chloride by shaking with freshly prepared silver chloride. Crystals of (+)<sub>D</sub>-[Co(en)<sub>3</sub>]Cl<sub>3</sub>.H<sub>2</sub>O, suitable for X-ray analysis were grown from an aqueous solution. They are very similar both in colour and shape to



and are orange-red prisms elongated along the  $c$  axis, in agreement with Jaeger's (1919) description. The crystals were reformed into cylinders, the axes of which were parallel to the  $c$  and  $a$  axes, respectively. They

easily lose the water of crystallization and disintegrate when exposed to air at room temperature. The specimens were protected from the atmosphere by a thin layer of grease during the X-ray exposure. In spite of this precaution measurements had to be made of a half-dozen cylindrical specimens of diameters ranging from 0.086 to 0.110 mm for the  $c$ -axis rotation and from 0.146 to 0.2 mm for the  $a$ -axis rotation. This would affect the accuracy of the measurement to some extent. Nickel filtered copper radiation was used. The intensity data for layers  $l=0$  through 12 and for  $h=0$  through 4 were recorded on multiple film, equi-inclination Weissenberg photographs, and relative intensities of the reflexions were obtained by visual comparison with a calibrated intensity scale. The relative intensity ranged from about  $10^5$  to unity. The usual  $L_p$  and spot shape corrections were made; absorption corrections were also applied (*International Tables for X-ray Crystallography*, 1959). 1358 independent  $|F(hkl)|$  were collected. Those reflexions which were non-equivalent as a result of anomalous dispersion were treated as independent reflexions.

The cell dimensions determined from Weissenberg photographs were refined by a least-squares method, by employing data obtained on a single-crystal diffractometer with Fe  $K\alpha$  radiation ( $\alpha_1=1.93597$ ,  $\alpha_2=1.93991$  Å). Zero point deviation of the diffractometer graduation was included in the least-squares calculation as an unknown parameter. The crystals are isostructural with [Co(en)<sub>3</sub>]Br<sub>3</sub>.H<sub>2</sub>O; the crystal data are:



F.W. = 363.6; tetragonal,  $a=9.682 \pm 0.002$ ,  $c=16.287 \pm 0.002$  Å,  $U=1526.8$  Å<sup>3</sup> (20°C);  $D_m=1.585$  g.cm<sup>-3</sup> (20°C),  $Z=4$ ,  $D_x=1.587$  g.cm<sup>-3</sup>; space group  $P4_32_12$  ( $D_4^8$ , No. 96);  $F(000)=760$ ; linear absorption coefficient for Cu  $K\alpha$ ,  $\mu=136.8$  cm<sup>-1</sup>.

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Table 1 (cont.)

H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>	H	K	L	F <sub>o</sub>	F <sub>c</sub>
12	1	1	351	353	10	10	0	0	0	221	228	228	228	228	6	8	4	170	148	8	8	7	0	0
13	1	1	108	108	10	10	0	0	0	182	182	182	182	182	8	8	4	182	115	8	8	1	1	1
14	1	1	166	187	10	10	0	0	0	800	800	800	800	800	8	8	4	183	202	8	8	9	9	9
15	1	1	187	184	10	10	0	0	0	165	165	165	165	165	8	8	4	65	224	8	8	10	10	10
16	1	1	62	62	10	10	0	0	0	148	148	148	148	148	8	8	4	0	59	8	8	11	11	11
17	1	1	128	128	10	10	0	0	0	91	115	219	228	228	8	8	4	0	32	8	8	12	12	12
18	1	1	89	84	10	10	0	0	0	110	110	287	237	234	8	8	4	0	77	8	8	13	13	13
19	1	1	131	131	10	10	0	0	0	136	136	204	169	169	8	8	4	0	75	8	8	14	14	14
20	1	1	82	84	10	10	0	0	0	110	115	154	161	161	8	8	4	0	77	8	8	15	15	15
21	1	1	281	301	10	10	0	0	0	99	98	204	169	169	8	8	4	0	85	8	8	16	16	16
22	1	1	691	678	10	10	0	0	0	151	151	154	161	161	8	8	4	0	77	8	8	17	17	17
23	1	1	183	183	10	10	0	0	0	151	151	213	213	213	8	8	4	0	77	8	8	18	18	18
24	1	1	66	104	10	10	0	0	0	99	128	113	134	134	8	8	4	0	216	8	8	19	19	19
25	1	1	251	242	10	10	0	0	0	111	111	111	123	123	8	8	4	0	207	8	8	20	20	20
26	1	1	108	118	10	10	0	0	0	111	111	111	123	123	8	8	4	0	60	8	8	21	21	21
27	1	1	112	145	10	10	0	0	0	145	161	64	91	91	8	8	4	0	171	8	8	22	22	22
28	1	1	361	346	10	10	0	0	0	145	161	64	91	91	8	8	4	0	171	8	8	23	23	23
29	1	1	188	188	10	10	0	0	0	145	161	64	91	91	8	8	4	0	171	8	8	24	24	24
30	1	1	31	28	10	10	0	0	0	112	141	123	139	139	8	8	4	0	57	8	8	25	25	25
31	1	1	51	105	10	10	0	0	0	70	70	154	115	115	8	8	4	0	231	8	8	26	26	26
32	1	1	245	240	10	10	0	0	0	70	70	154	115	115	8	8	4	0	231	8	8	27	27	27
33	1	1	86	96	10	10	0	0	0	98	98	127	127	127	8	8	4	0	143	8	8	28	28	28
34	1	1	195	195	10	10	0	0	0	543	543	10	10	10	8	8	4	0	47	8	8	29	29	29
35	1	1	282	282	10	10	0	0	0	151	151	10	10	10	8	8	4	0	96	8	8	30	30	30
36	1	1	745	745	10	10	0	0	0	151	151	10	10	10	8	8	4	0	96	8	8	31	31	31
37	1	1	295	295	10	10	0	0	0	251	251	10	10	10	8	8	4	0	101	8	8	32	32	32
38	1	1	137	137	10	10	0	0	0	267	267	10	10	10	8	8	4	0	440	8	8	33	33	33
39	1	1	345	345	10	10	0	0	0	167	167	10	10	10	8	8	4	0	402	8	8	34	34	34
40	1	1	770	749	10	10	0	0	0	237	265	10	10	10	8	8	4	0	233	8	8	35	35	35
41	1	1	113	114	10	10	0	0	0	186	210	10	10	10	8	8	4	0	246	8	8	36	36	36
42	1	1	556	556	10	10	0	0	0	202	202	10	10	10	8	8	4	0	165	8	8	37	37	37
43	1	1	188	188	10	10	0	0	0	251	251	10	10	10	8	8	4	0	165	8	8	38	38	38
44	1	1	186	205	10	10	0	0	0	251	251	10	10	10	8	8	4	0	165	8	8	39	39	39
45	1	1	108	108	10	10	0	0	0	267	267	10	10	10	8	8	4	0	165	8	8	40	40	40
46	1	1	1316	1316	10	10	0	0	0	416	416	10	10	10	8	8	4	0	165	8	8	41	41	41
47	1	1	256	277	10	10	0	0	0	368	362	10	10	10	8	8	4	0	165	8	8	42	42	42
48	1	1	170	170	10	10	0	0	0	378	378	10	10	10	8	8	4	0	165	8	8	43	43	43
49	1	1	269	266	10	10	0	0	0	405	348	10	10	10	8	8	4	0	165	8	8	44	44	44
50	1	1	127	118	10	10	0	0	0	347	348	10	10	10	8	8	4	0	165	8	8	45	45	45
51	1	1	454	454	10	10	0	0	0	159	159	10	10	10	8	8	4	0	165	8	8	46	46	46
52	1	1	375	375	10	10	0	0	0	157	157	10	10	10	8	8	4	0	165	8	8	47	47	47
53	1	1	180	180	10	10	0	0	0	180	232	10	10	10	8	8	4	0	165	8	8	48	48	48
54	1	1	254	250	10	10	0	0	0	303	303	10	10	10	8	8	4	0	165	8	8	49	49	49
55	1	1	181	181	10	10	0	0	0	6	6	10	10	10	8	8	4	0	165	8	8	50	50	50
56	1	1	285	285	10	10	0	0	0	17	17	10	10	10	8	8	4	0	165	8	8	51	51	51
57	1	1	155	180	10	10	0	0	0	373	403	10	10	10	8	8	4	0	165	8	8	52	52	52
58	1	1	172	172	10	10	0	0	0	373	403	10	10	10	8	8	4	0	165	8	8	53	53	53
59	1	1	202	202	10	10	0	0	0	411	429	10	10	10	8	8	4	0	165	8	8	54	54	54
60	1	1	189	202	10	10	0	0	0	115	79	10	10	10	8	8	4	0	165	8	8	55	55	55
61	1	1	141	168	10	10	0	0	0	681	681	10	10	10	8	8	4	0	165	8	8	56	56	56
62	1	1	180	161	10	10	0	0	0	431	452	10	10	10	8	8	4	0	165	8	8	57	57	57
63	1	1	144	144	10	10	0	0	0	246	216	10	10	10	8	8	4	0	165	8	8	58	58	58
64	1	1	55	55	10	10	0	0	0	0	0	10	10	10	8	8	4	0	165	8	8	59	59	59
65	1	1	94	94	10	10	0	0	0	0	0	10	10	10	8	8	4	0	165	8	8	60	60	60
66	1	1	181	181	10	10	0	0	0	266	281	10	10	10	8	8	4	0	165	8	8	61	61	61
67	1	1	88	88	10	10	0	0	0	357	357	10	10	10	8	8	4	0	165	8	8	62	62	62
68	1	1	75	109	10	10	0	0	0	200	217	10	10	10	8	8	4	0	165	8	8	63	63	63
69	1	1	112	112	10	10	0	0	0	120	120	10	10	10	8	8	4	0	165	8	8	64	64	64
70	1	1	18	18	10	10	0	0	0	3	3	10	10	10	8	8	4	0	165	8	8	65	65	65
71	1	1	261	261	10	10	0	0	0	14	187	218	218	218	8	8	4	0	165	8	8	66	66	66
72	1	1	563	558	10	10	0	0	0	152	176	176	176	176	8	8	4	0	165	8	8	67	67	67
73	1	1	330	329	10	10	0	0	0	107	107	10	10	10	8	8	4	0	165	8	8	68	68	68
74	1	1	211	211	10	10	0	0	0	177	177	10	10	10	8	8	4	0	165	8	8	69	69	69
75	1	1	354	354	10	10	0	0	0	181	181	10	10	10	8	8	4	0	165	8	8	70	70	70
76	1	1	268	263	10	10	0	0	0	160	160	10	10	10	8	8	4	0	165	8	8	71	71	71
77	1	1	221	221	10	10	0	0	0	141	141	10	10	10	8	8	4	0	165	8	8	72	72	72
78	1	1	244	253	10	10	0	0	0	133	148	10	10	10	8	8	4	0	165	8	8	73	73	73
79	1	1	231	231	10	10	0	0	0	168	168	10	10	10	8	8	4	0	165	8	8	74	74	74
80	1	1	247	247	10	10	0	0	0	154	154	10	10	10	8	8	4	0	165	8	8	75	75	75

proximate positions of the hydrogen atoms except that attached to C(2). At this stage it was felt desirable to adopt a new weighting scheme with some down weighting of very weak and very strong reflexions. The new scheme, a modification of Cruickshank's method (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), was as follows:  $1/w = c - |F_o| + a|F_o|^2$  if  $|F_o| \leq F_{\min}$  and  $|F_o| \geq F_{\max}$ ; otherwise  $1/w = d$ . The coefficients  $a$ ,  $c$ , and

$d$  were determined so as to give an approximately constant average value of  $w|\Delta F|^2$  in each intensity region and to give a maximum value of  $w$  in the region,  $25.0 \leq |F_o| \leq 85.0$ . After these corrections and the introduction of hydrogen atoms obtained from the difference synthesis (the missing hydrogen atom attached to C(2) was supplied by the calculated value), a final set of least-squares calculations was carried out. A total of three cycles was computed before the shifts were less than the standard deviations for non-hydrogen atoms. Temperature factors of hydrogen atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were bonded. In the last cycle of least-squares, no coordinate shift of non-hydrogen atoms exceeded  $0.003 \text{ \AA}$  or  $0.5 \sigma$ , and the average shift was about  $0.15$  times the estimated standard deviations. The average hydrogen coordinate shift was  $0.65 \sigma$  and the maximum shift was  $0.1 \text{ \AA}$  or  $1.0 \sigma$  for H(water). The topography of the final difference synthesis is flat, within the range of  $\pm 0.9 \text{ e.\AA}^{-3}$ .

Table 1 gives the observed and calculated structure factors. The final  $R$  was  $0.090$ . The final atomic parameters are shown in Table 2 together with e.d.s.'s obtained from the inverse matrix of the normal equation matrix of least-squares. If the structure is inverted, the  $R$  value increases by about  $0.06$ .

### Computing procedures

The reduction of the original data, preliminary calculations of structure factors and all other calculations not mentioned in the following were carried out on the

Table 2. Atomic parameters

Standard deviations in parentheses.

(a) Positional parameters ( $\times 10^4$ )

	$x/a$	$y/b$	$z/c$
Co	4797 (1)	5203 (1)	2500
Cl(1)	9510 (1.8)	490 (1.8)	2500
Cl(2)	3542 (2)	969 (2)	2494 (2)
O	1909 (5.7)	8091 (5.7)	2500
C(1)	6757 (11)	3216 (12)	2967 (4)
C(2)	2038 (10)	4379 (10)	2145 (6)
C(3)	2114 (9)	4565 (11)	3058 (5)
N(1)	5352 (7)	3657 (7)	3199 (4)
N(2)	3481 (6)	4019 (7)	1877 (3)
N(3)	3205 (7)	5634 (7)	3212 (5)
H(O)	1148 (108)	7905 (109)	2625 (83)
H(C11)	7316 (112)	4024 (110)	3220 (69)
H(C12)	6672 (100)	2301 (116)	3138 (64)
H(C21)	1889 (100)	5433 (107)	1777 (57)
H(C22)	1402 (102)	3572 (105)	1971 (62)
H(C31)	1178 (101)	4828 (97)	3206 (54)
H(C32)	2336 (98)	3696 (95)	3359 (57)
H(N11)	5545 (94)	3921 (88)	3681 (57)
H(N12)	4428 (105)	3075 (98)	3110 (58)
H(N21)	3746 (94)	3007 (104)	2124 (51)
H(N22)	3949 (90)	4100 (96)	1344 (54)
H(N31)	3004 (102)	6627 (100)	3027 (55)
H(N32)	3269 (104)	5359 (97)	3742 (57)

Table 2 (cont.)

(b) Thermal parameters ( $\times 10^5$ )

Based on  $B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl$ .

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co	533 (13)	533 (13)	186 (4)	-8 (15)	20 (6)	20 (6)
Cl(1)	1255 (26)	1255 (26)	226 (8)	425 (33)	-9 (17)	-9 (17)
Cl(2)	1329 (29)	600 (22)	410 (7)	-57 (22)	-10 (19)	85 (16)
O	886 (70)	886 (70)	673 (47)	123 (97)	90 (60)	90 (60)
C(1)	850 (128)	1108 (146)	289 (31)	350 (97)	6 (58)	8 (63)
C(2)	882 (115)	824 (127)	316 (34)	-63 (103)	8 (51)	-121 (51)
C(3)	516 (98)	894 (112)	260 (32)	-195 (102)	-7 (45)	-22 (52)
N(1)	522 (70)	612 (75)	194 (21)	-37 (72)	-44 (38)	23 (34)
N(2)	649 (79)	635 (74)	157 (21)	-264 (70)	53 (35)	-39 (35)
N(3)	645 (82)	731 (96)	243 (25)	-125 (73)	86 (40)	-40 (41)

$B^*$

H(O)	4.4 $\text{\AA}^2$
H(C11)	3.8
H(C12)	3.8
H(C21)	3.3
H(C22)	3.3
H(C31)	2.7
H(C32)	2.7
H(N11)	2.1
H(N12)	2.1
H(N21)	2.2
H(N22)	2.2
H(N31)	2.6
H(N32)	2.6

\* Isotropic, and given the same values as those of the atoms to which the hydrogen atoms are bonded.

Table 3. Intermolecular approaches\* less than 4 Å

The superscripts designate:

No symbol	x	y	z
( <sup>i</sup> )	1-y	1-x	$\frac{1}{2}$ -z
( <sup>ii</sup> )	$\frac{3}{2}$ -x	$\frac{1}{2}$ +y	$\frac{3}{2}$ -z
( <sup>iii</sup> )	-y	1-x	$\frac{1}{2}$ -z
(iv)	-y	2-x	$\frac{1}{2}$ -z
(v)	$\frac{1}{2}$ -y	$-\frac{1}{2}$ +x	$-\frac{1}{4}$ +z
(vi)	$\frac{1}{2}$ -x	$\frac{1}{2}$ +y	$\frac{3}{4}$ -z
(vii)	$\frac{1}{2}$ +y	$\frac{1}{2}$ -x	$\frac{1}{4}$ +z
(viii)	$\frac{1}{2}$ -x	$-\frac{1}{2}$ +y	$\frac{3}{4}$ -z
(ix)	$-\frac{1}{2}$ +y	$\frac{1}{2}$ -x	$\frac{1}{4}$ +z
(x)	x	1+y	z

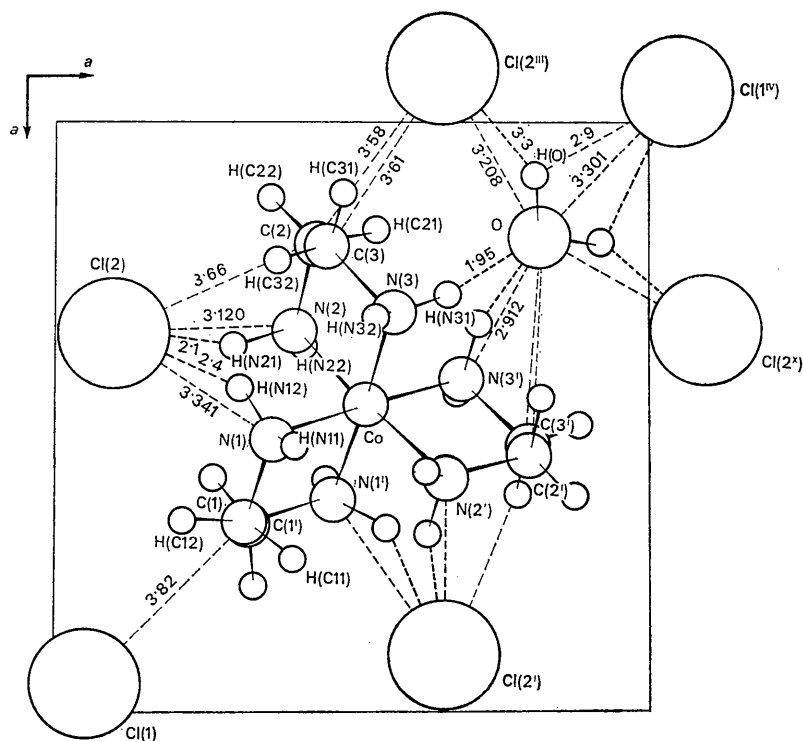
  

C(1)···Cl(1)	3·824 (11) Å	C(3)···Cl(2''')	3·611 (9) Å
C(1)···Cl(2)	3·879 (11)	C(3)···Cl(2 <sup>v</sup> )	3·507 (9)
C(1)···Cl(2 <sup>vii</sup> )	3·792 (9)	C(3)···O	3·527 (12)
C(1)···Cl(2')	3·905 (12)	C(3)···O <sup>ix</sup>	3·599 (9)
C(2)···Cl(2)	3·656 (10)	N(1)···Cl(2 <sup>vii</sup> )	3·663 (7)
C(2)···Cl(2''')	3·582 (10)	N(1)···O <sup>viii</sup>	3·709 (8)
C(2)···O	3·631 (11)	N(3)···Cl(1')	3·662 (7)
C(3)···Cl(2)	3·860 (10)	N(3)···O <sup>viii</sup>	3·822 (8)

A-H···B	A···B	H···B	∠(A-H···B)
N(1)-H(N12)···Cl(2)	3·341 (7) Å	2·43 (10) Å	143 (7) <sup>o</sup>
N(1)-H(N11)···Cl(1')	3·431 (6)	2·63 (9)	158 (8)
N(2)-H(N21)···Cl(2)	3·120 (7)	2·07 (10)	160 (8)
N(2)-H(N22)···Cl(1 <sup>v</sup> )	3·250 (6)	2·29 (9)	165 (7)
N(3)-H(N31)···O	2·912 (9)	1·95 (10)	155 (8)
N(3)-H(N32)···Cl(2 <sup>v</sup> )	3·387 (8)	2·76 (10)	127 (8)
O-H(O)···Cl(2''')	3·208 (6)	3·32 (12)	149 (10)
O-H(O)···Cl(1 <sup>v</sup> )	3·301 (6)	2·91 (12)	104 (8)

\* Corrected for thermal motion (Cruickshank, 1956b).

Fig. 1. Atomic arrangement viewed along the *c* axis near  $z = \frac{1}{4}$ . Dotted lines indicate close contacts.

FACOM 202 computer at this Institute. Interlayer corrections, least-squares calculations and the Fourier synthesis were computed on the HITAC 5020 at the Computing Centre of the University with the programs *RSC 3*, *FLS 4* and *ANSR-1* respectively, of the *UNICS* system written by Dr T. Sakurai and Dr. H. Iwasaki with slight modifications in the weighting scheme and damping factors of the parameter shifts, *etc.* by one of the authors (M.I.).

### Results and discussion

#### Packing and geometry of the complex ion

The overall structure is the same as that of the isostructural bromide, (+)<sub>D</sub>-[Co(en)<sub>3</sub>]Br<sub>3</sub>·H<sub>2</sub>O (Nakatsu, 1962). A partial projection of the structure around  $z = \frac{1}{4}$  down the *c* axis is shown in Fig. 1. Fig. 2 illustrates packing relations around a complex ion. Table 3 lists some of the important interatomic distances and angles outside the complex ion. The distances between each chloride ion and its nearest neighbour are found to be shorter by about 0.12 Å than the corresponding dis-

tances in the bromide. This decrease is primarily the result of the difference in the ionic radii of Cl<sup>-</sup> and Br<sup>-</sup>.

Three types of hydrogen bond are conceivable, *i.e.* N-H...O, O-H...Cl<sup>-</sup> and N-H...Cl<sup>-</sup>. The first type, N-H...O, is found between N(3) and O with length 2.91 Å. Two hydrogen atoms of the water molecule are oriented towards Cl<sup>-</sup>(2'') and Cl<sup>-</sup>(2<sup>x</sup>) of the adjacent unit cell, forming the second type, O-H...Cl<sup>-</sup> with the same length 3.21 Å, for each; this type of weak hydrogen bond is reported for CuCl<sub>2</sub>·2H<sub>2</sub>O (Peterson & Levy, 1957). The third type, N-H...Cl<sup>-</sup>, probably exists between N(2) and Cl<sup>-</sup>(2), N(2) and Cl<sup>-</sup>(1<sup>v</sup>), N(1) and Cl<sup>-</sup>(2), and N(1) and Cl<sup>-</sup>(1'') in decreasing order of strength (see Table 3). These N...Cl<sup>-</sup> distances and N-H-Cl angles are 3.120, 3.250, 3.341 and 3.431 Å, and 160, 165, 143 and 158°, respectively. Other close contacts occur between amino nitrogen atoms of the complex ion and chloride ions, as listed in Table 3.

As for the geometry of the complex ion, no significant change was found from the previous results. Table 4 lists the interatomic distances and bond angles within the complex ion [Co(en)<sub>3</sub>]<sup>3+</sup>. The symmetry of the com-

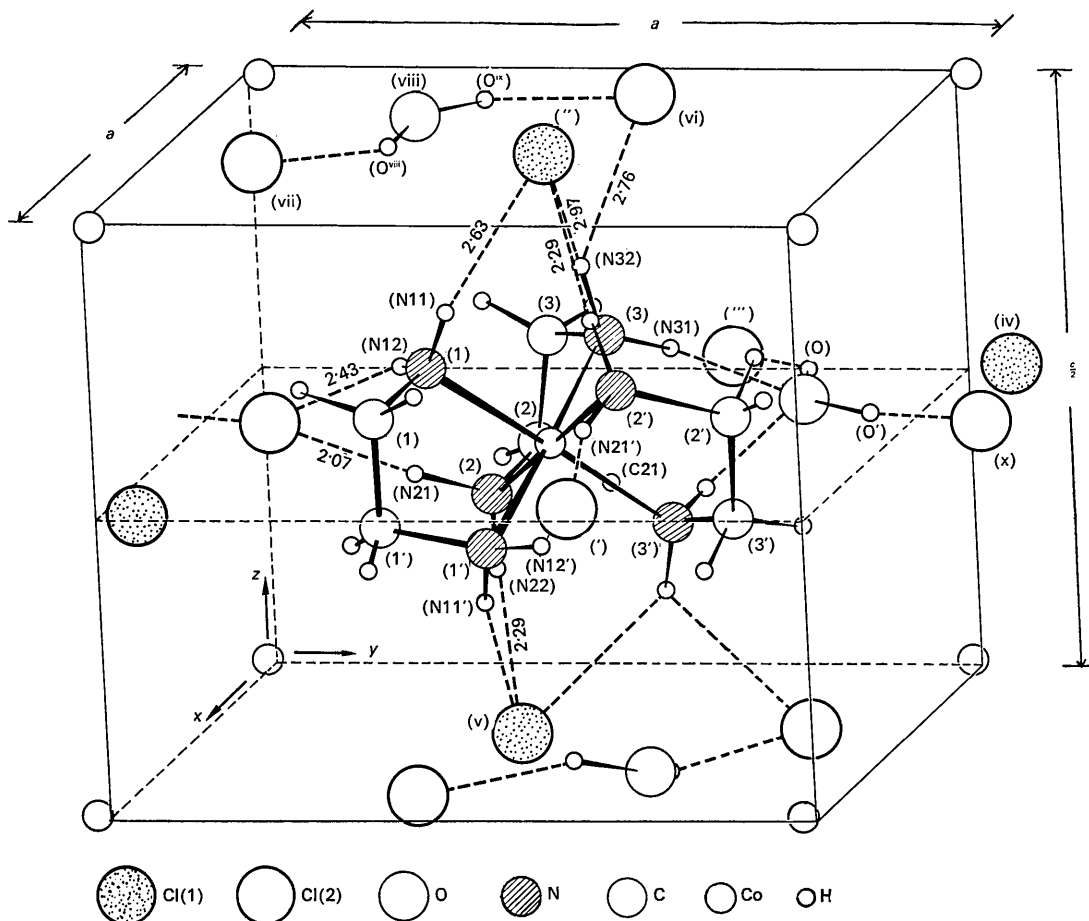


Fig. 2. Atomic arrangement (from  $z = 0$  to  $z = \frac{1}{4}$ ) around the complex ion. Dotted lines lead to neighbouring atoms of the hydrogen atoms but do not necessarily represent hydrogen bonds.

plex ion as required by the space group is  $C_2-2$ . However, if the complex ion alone is considered, its symmetry can be represented approximately by  $D_3-322$ . Its quasi threefold axis of rotation is nearly parallel to the  $c$  axis, making an angle of  $3.2^\circ$  with it. The six nitrogen atoms of the ligand molecules form an octahedron around the central cobalt atom. The Co...N distances are 1.959, 1.996 and 1.979 Å (average  $1.978 \pm 0.004$  Å), in good agreement with the values obtained for other  $[\text{Co}(\text{en})_3]^{3+}$  salts. The average N-Co-N angle is  $85.3 \pm 0.3^\circ$ . Thus the displacements of these nitrogen atoms from the regular octahedral position is small. Fig. 3 shows the coordination octahedron viewed down the threefold axis. The triangle drawn by dotted lines shows the upper face of a regular octahedron, to which the plane defined by N(1), N(2') and N(3) is found to be rotated by  $\sim 5^\circ$ , as shown in the Figure. One of the three ethylenediamine molecules is characterized by the twofold rotational symmetry of the crystal, while the other two are disposed symmetrically to the same symmetry axis. Both kinds of ethylenediamine molecule are of the *gauche* form, and all three C-C bonds point along the threefold axis of the octahedron. Hence the conformations of the chelate rings are of the type *lel-lel*

(Corey & Bailar, 1959). The chelate rings are not planar: C(1) and C(1') are found to lie 0.376 Å above and below the plane of Co, N(1) and N(1'); C(2) lies 0.337 Å above and C(3) 0.414 Å below the plane of Co, N(2) and N(3). The absolute configuration of the complex ion agrees with the previous results (Saito, Nakatsu, Shiro & Kuroya, 1955, 1957; Nakatsu, 1962).

The three hydrogen atoms bound to nitrogen atoms of the upper (or lower) face of the octahedron are oriented nearly parallel to the threefold axis of the complex ion and they are on average about 2.4 Å apart, which corresponds to the O-O distances in such oxy-anions as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  or  $\text{SeO}_4^{2-}$ . This fact strongly supports the possibility of the complex ion forming ion pairs with those oxy-anions in solution by hydrogen bonds (Mason & Norman, 1964, 1965; Larsson, Mason & Norman, 1966).

#### Analysis of the thermal motions

The anisotropic thermal parameters [Table 2(b)] of the non-hydrogen atoms of the  $[\text{Co}(\text{en})_3]^{3+}$  ion were used in an analysis of the rigid-body translational and librational motion by assuming the centre of motion to be at the central cobalt atom (Cruickshank, 1956a).

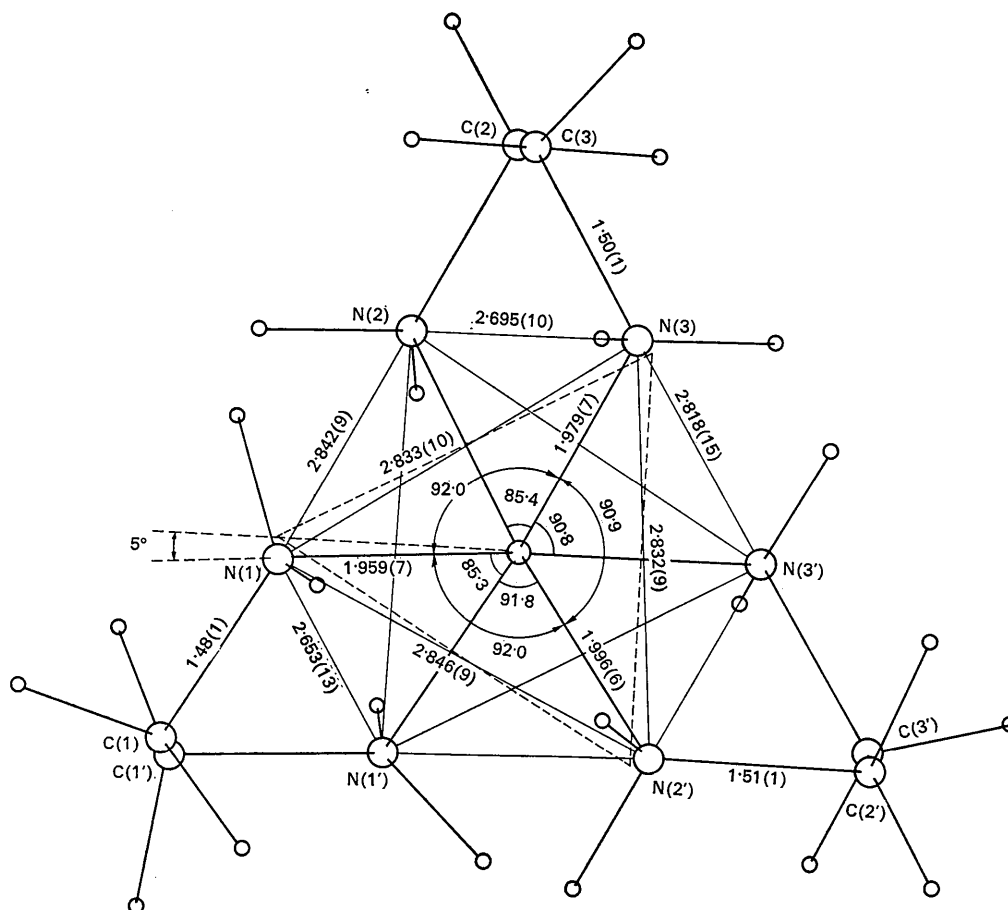


Fig. 3. Geometry of the complex ion viewed down the threefold axis.

Table 5 lists the root-mean-square amplitudes of the principal axes of the  $T$  and  $\omega$  ellipsoids (Cruickshank's notation). These translational and librational amplitudes were small and not significantly anisotropic, averaging about 0.16 Å and 2.6° respectively. The coupling of the motions of neighbouring atoms and the presence of hydrogen bonding appears to preclude large libration or translation, and hence the largest observed eigenvalues of  $T$  and  $\omega$  are only 0.17 Å and 3.1° respectively. Consequently the corrections to the interatomic distances for rotational motion (Cruickshank, 1956*b*) were found to be within their standard deviations. In Table 6, the observed  $U_{ij}$ 's ( $= B_{ij}/2\pi^2 a_i^* a_j^*$ ) are compared with the values calculated from  $T$ ,  $\omega$  and atomic coordinates based on the assumption that the whole ion is a rigid body. The r.m.s. discrepancy between the observed and calculated  $U_{ij}$  for the ion is  $1.3 \times 10^{-2}$  Å<sup>2</sup>, a value whose magnitude indicates some internal motion. The observed  $U_{ij}$ 's are diagonalized and the resultant thermal ellipsoids are shown in Table 7 and in Fig. 4 for one chelate ring [Co, N(1), C(1), C(1'), N(1')]. It can be seen from Table 7 that the vib-

ration of the central cobalt atom is nearly isotropic. The carbon atoms of the chelate rings appear to oscillate with large amplitudes nearly perpendicularly to the C—C bond; the carbon atom C(1) has the largest amplitude. However, the vibrations of the other carbon atoms are relatively small. This is a result of the presence of the chloride ions at distances 3.582 and 3.507 Å from these carbon atoms. The chloride ions seem to hinder such vibrations of the carbon atoms. On the other hand the C(1) . . . Cl distance is 3.792 Å, which is large enough to allow such vibrations of the carbon atoms. A similar type of vibration has already been reported (for example, C<sub>4</sub>H<sub>8</sub>Se, Pedersen & Hope, 1965). These features of the anisotropic vibrations of the carbon atoms seem to support the existence of a puckering motion of the chelate ring in solution. Actually Mason & Norman (1964, 1965) measured the circular dichroism spectra of [Co(en)<sub>3</sub>]<sup>3+</sup> ions in solution and suggested that different conformations of [Co(en)<sub>3</sub>]<sup>3+</sup> coexist in solution (McCaffery, Mason & Norman, 1965); this was supported by the thermodynamic data (Dwyer, Garvan & Shulman, 1959).

Table 4. Bond lengths and angles corrected for thermal motion\*

E.s.d. in parentheses for least significant figures.

Co—N(1)	1.959 (7) Å	N(1)—C(1)—H(C11)	100 (6)°
Co—N(2)	1.996 (6)	N(1)—C(1)—H(C12)	97 (7)
Co—N(3)	1.979 (7)	H(C11)—C(1)—H(C12)	130 (9)
		H(C11)—C(1)—C(1')	112 (7)
C(1)—N(1)	1.48 (1)	H(C12)—C(1)—C(1')	108 (8)
C(2)—N(2)	1.51 (1)		
C(3)—N(3)	1.50 (1)	C(3)—C(2)—H(C21)	114 (5)
		C(3)—C(2)—H(C22)	113 (6)
C(1)—C(1')	1.52 (1.5)	N(2)—C(2)—H(C21)	100 (5)
C(2)—C(3)	1.50 (1)	N(2)—C(2)—H(C22)	108 (6)
		H(C21)—C(2)—H(C22)	116 (7)
C(1)—H(C11)	1.04 (11)		
C(1)—H(C12)	0.94 (11)	C(2)—C(3)—H(C31)	103 (6)
C(2)—H(C21)	1.19 (10)	C(2)—C(3)—H(C32)	113 (5)
C(2)—H(C22)	1.04 (10)	N(3)—C(3)—H(C31)	116 (6)
C(3)—H(C31)	0.98 (10)	N(3)—C(3)—H(C32)	110 (5)
C(3)—H(C32)	1.00 (9)	H(C31)—C(3)—H(C32)	107 (8)
N(1)—H(N11)	0.85 (9)		
N(1)—H(N12)	1.07 (10)	Co—N(1)—H(N11)	112 (6)
N(2)—H(N21)	1.09 (10)	Co—N(1)—H(N12)	95 (5)
N(2)—H(N22)	0.98 (9)	C(1)—N(1)—H(N11)	97 (6)
N(3)—H(N31)	1.03 (10)	C(1)—N(1)—H(N12)	126 (5)
N(3)—H(N32)	0.91 (9)	H(N11)—N(1)—H(N12)	118 (8)
O—H(O)	0.99 (11)		
		Co—N(2)—H(N21)	100 (5)
N(1)—Co—N(1')	85.3 (3)°	Co—N(2)—H(N22)	96 (5)
N(2)—Co—N(3)	85.4 (3)	C(2)—N(2)—H(N21)	109 (5)
		C(2)—N(2)—H(N22)	132 (5)
Co—N(1)—C(1)	109.0 (6)	H(N21)—N(2)—H(N22)	107 (7)
Co—N(2)—C(2)	108.3 (5)		
Co—N(3)—C(3)	107.9 (6)	Co—N(3)—H(N31)	100 (5)
		Co—N(3)—H(N32)	116 (6)
C(1')—C(1)—N(1)	105.4 (7)	C(3)—N(3)—H(N31)	118 (5)
C(3)—C(2)—N(2)	105.7 (7)	C(3)—N(3)—H(N32)	90 (6)
C(2)—C(3)—N(3)	106.4 (7)	H(N31)—N(3)—H(N32)	125 (8)
H(O)—O—H(O')	118 (9)	Dihedral angle	
		N(1)—C(1)—C(1')—N(1')	54.5°
		N(2)—C(2)—C(3)—N(3)	55.6

\* Cruickshank (1956*b*)



Table 5. *Rigid-body thermal parameters*

R.m.s. amplitude of translational motion	Direction cosine of principal axes of $T$ relative to the crystal axes		
0.165 Å	0.7122	-0.7016	-0.0019
0.159	0.3820	0.3636	0.8498
0.155	0.5900	0.6119	-0.5268

R.m.s. amplitude of angular libration	Direction cosine of principal axes of $\omega$ relative to the crystal axes		
2.6°	0.6912	0.7107	-0.1313
1.9	0.7187	-0.6951	0.0129
3.3	0.0822	0.1032	0.9913

The largest and smallest amplitudes of vibration of the chloride ions Cl(1) and Cl(2) are in the approximate directions [110] and [001], and [100] and [010], respectively. This is because the packing of adjacent atoms is loosest and closest in these directions respectively.

The oxygen atom of the water molecule has the largest amplitude of all the atoms in the crystal along [001]. In other words, the water molecule moves fairly freely along the tunnel formed by the chloride ions and the complex ions. In fact, the crystal easily loses its water of crystallization. The crystals can be partly

dehydrated on standing in air without there being any remarkable change in their appearance. These partly dehydrated crystals give well-defined single-crystal diffraction patterns, and some of them show superstructure reflexions along the  $a$  axis ( $2 \times a$ ).

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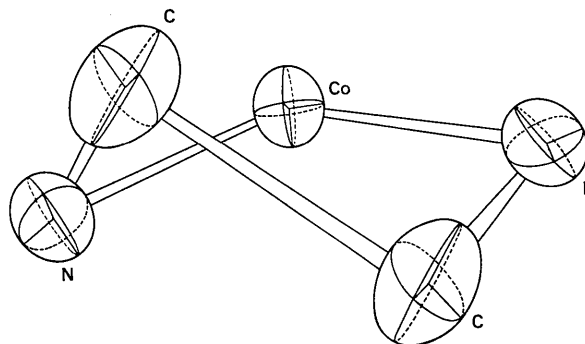


Fig.4 Thermal motion of the chelate ring Co, N(1), C(1), C(1'), N(1').

Table 6. *Comparison of observed and calculated thermal parameters ( $\times 10^5 \text{ \AA}^2$ )*

E.s.d.'s in parentheses.

		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	obs.	2630 (62)	2630 (62)	2505 (54)	-37 (71)	158 (48)	158 (48)
	calc.	2576	2576	2489	-147	43	43
C(1)	obs.	4035 (608)	5262 (693)	3878 (417)	1663 (461)	51 (463)	67 (503)
	calc.	3930	3810	3971	1030	-344	247
C(2)	obs.	4186 (546)	3914 (603)	4249 (457)	-302 (489)	62 (407)	-963 (407)
	calc.	2827	4918	3522	-829	-166	-37
C(3)	obs.	2450 (465)	4247 (532)	3491 (430)	-926 (484)	-59 (359)	-175 (415)
	calc.	2856	4946	3476	-740	402	-53
N(1)	obs.	2480 (332)	2906 (356)	2609 (282)	-173 (342)	-350 (304)	182 (272)
	calc.	3568	2854	2958	55	-170	328
N(2)	obs.	3082 (375)	3013 (351)	2110 (282)	-1255 (332)	422 (280)	-311 (280)
	calc.	3145	3232	2812	-634	-112	-85
N(3)	obs.	3062 (389)	3472 (456)	3262 (336)	-593 (347)	685 (320)	-333 (328)
	calc.	2835	3586	2948	-15	331	-156

Table 7. *Vibrational amplitudes and the direction cosines of the principal axes relative to the crystal axes*

Co	0.152 Å	0.4519	0.4519	-0.7691	C(2)	0.175 Å	0.1729	0.7671	0.6178
	0.163	0.7072	-0.7071	0.0001		0.204	0.9515	0.0321	-0.3061
	0.167	0.5438	0.5438	0.6392		0.226	0.2545	-0.6407	0.7243
Cl(1)	0.174	0.0145	0.0145	0.9998	C(3)	0.143	0.9159	0.3924	0.0851
	0.199	0.7071	-0.7071	0.0000		0.187	0.1244	-0.0758	-0.9893
	0.282	0.7070	0.7070	-0.0206		0.216	0.3818	-0.9167	0.1182
Cl(2)	0.163	0.0673	0.9708	-0.2304	N(1)	0.148	0.7741	0.0264	0.6325
	0.238	0.2031	0.2128	0.9558		0.163	0.4361	0.7018	-0.5633
	0.252	0.9768	-0.1111	-0.1828		0.178	0.4587	-0.7119	-0.5317
O	0.190	0.7071	-0.7071	0.0000	N(2)	0.133	0.7086	0.6425	-0.2917
	0.214	0.6896	0.6896	-0.2210		0.142	0.0563	0.3606	0.9310
	0.305	0.1563	0.1563	0.9753		0.210	0.7034	-0.6761	0.2194
C(1)	0.170	0.8205	-0.5717	-0.0036	N(3)	0.155	0.8008	0.2790	-0.5299
	0.197	0.0160	0.0292	-0.9995		0.175	0.1663	0.7465	0.6443
	0.254	0.5715	0.8200	0.0331		0.208	0.5754	-0.6041	0.5541

## References

- COREY, E. J. & BAILAR, J. C. JR (1959). *J. Amer. Chem. Soc.* **81**, 2620.
- CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 754.
- CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 757.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
- DWYER, F. P., GARVAN, F. L. & SHULMAN, L. (1959). *J. Amer. Chem. Soc.* **81**, 290.
- International Tables for X-ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JAEGER, F. M. (1919). *Z. Kristallogr.* **55**, 207.
- LARSSON, R., MASON, S. F. & NORMAN, B. J. (1966). *J. Chem. Soc. A*, p. 301.
- MASON, S. F. & NORMAN, B. J. (1964). *Proc. Chem. Soc.* p. 339;
- MASON, S. F. & NORMAN, B. J. (1965). *Chem. Comm.* p. 73.
- MCCAFFERY, A. J., MASON, S. F. & NORMAN, B. J. (1965). *Chem. Comm.* p. 49.
- NAKATSU, K. (1962). *Bull. Chem. Soc. Japan*, **35**, 832.
- NAKATSU, K., SAITO, Y. & KUROYA, H. (1956). *Bull. Chem. Soc. Japan*, **29**, 428.
- NAKATSU, K., SHIRO, M., SAITO, Y. & KUROYA, H. (1957). *Bull. Chem. Soc. Japan*, **30**, 158.
- PEDERSEN, B. & HOPE, H. (1965). *Acta Cryst.* **19**, 473.
- PETERSON, S. W. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 2200.
- PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173.
- SAITO, Y., NAKATSU, K., SHIRO, M. & KUROYA, H. (1955). *Acta Cryst.* **8**, 729.
- SAITO, Y., NAKATSU, K., SHIRO, M. & KUROYA, H. (1957). *Bull. Chem. Soc. Japan*, **30**, 795.
- WERNER, A. (1912). *Ber. dtsh. chem. Ges.* **45**, 128.

*Acta Cryst.* (1969). **B25**, 2571

## The Use of Non-Crystallographic Symmetry for Phase Determination

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When a crystal contains more than one identical molecule or sub-unit in the crystallographic asymmetric unit, the structure factors must satisfy a set of complex linear equations. Given a set of structure amplitudes for a structure with the postulated non-crystallographic symmetry, the particular nature of the eigenvalue spectrum of the matrix of the equations provides a formal basis for an iterative procedure for generating the phases of the structure factors from the equations. The method has been tested on a number of model structures. An estimate is given of how strong the non-crystallographic symmetry constraints must be in order to generate a unique set of phases.

### Introduction

In a previous paper (Crowther, 1967) it was shown that the structure-factor equations, which may be constructed when a crystal contains more than one identical molecule or sub-unit within the crystallographic asymmetric unit (Main & Rossmann, 1966), can be written in the form

$$\mathbf{H}\mathbf{F} = \mathbf{F} \quad (1)$$

Here  $\mathbf{F}$  is a vector whose elements are the complex structure factors out to the resolution to which we are working and  $\mathbf{H}$  is a hermitian matrix ( $H_{rs} = H_{sr}^*$ , where the asterisk denotes complex conjugate) describing the relative geometry of the sub-units. The elements of  $\mathbf{H}$  are expressed in terms of the rotations and translations relating the various sub-units, which we assume are known, so that the elements of  $\mathbf{H}$  can be evaluated numerically for any given arrangement of sub-units.

Any eigenvector of the matrix  $\mathbf{H}$  corresponding to a unit eigenvalue is a possible solution of (1) and conversely the number of independent solutions of (1) is

equal to the number of unit eigenvalues of the matrix  $\mathbf{H}$ . The Fourier transform of the particular set of structure factors constituting an eigenvector of  $\mathbf{H}$  will be called an eigendensity. Eigenvectors and eigendensities corresponding to unit eigenvalues will be termed 'allowed'. Any structure with the postulated non-crystallographic symmetry may, to the resolution to which we are working, be expressed as a linear combination of the allowed eigendensities and correspondingly its transform may be expressed as a linear combination of the allowed eigenvectors. The allowed eigendensities form a more appropriate set of functions in which to expand a density with non-crystallographic symmetry than the more normally used Fourier terms.

Turning now to structure determination, let us take an unknown structure with known non-crystallographic symmetry. The question we pose is whether, given a set of measured structure amplitudes, it is possible to use the constraints introduced by non-crystallographic symmetry to solve the structure. For simplicity we take the space group to be  $P1$  and let us suppose that  $(2N+1)$  reflexions are to be included,