Table 8 (*cont.*)

$C(12)\cdots C(18^{ix})$	3·98
$C(12)\cdots O(1^{ix})$	3·61
$C(13)\cdots C(15^{ix})$	3·60
$C(13)\cdots C(16^{ix})$	3·84
$C(13)\cdots C(17^{ix})$	3·94
$C(13)\cdots C(18^{ix})$	3·72
$C(14)\cdots C(23^{x})$	3·72
$C(18)\cdots C(21^{ii})$	3·99
$C(21)\cdots C(21^{vi})$	3·42
$C(22)\cdots C(22^{iv})$	3·81
$C(23)\cdots O(2^{vii})$	3·84

Symmetry code

Superscript	Symmetry operator		
i	x	y	z
ii	$1+x$	y	z
iii	$-1+x$	y	z
iv	x	$1-y$	$2-z$
v	$-x$	y	$\frac{3}{2}-z$
vi	$-1-x$	y	$\frac{3}{2}-z$
vii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
viii	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	z
ix	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
x	$-\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
xi	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$2-z$

The absolute configuration determined in the present analysis is 1*R*6*S*, while the structure deduced by the theory of optical rotation is the opposite of this result. The cause of this disagreement will be studied further and will be discussed in a separate paper.

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The Crystal Structure of Potassium $(-)_{589}$-Tris(1,2-benzenediolato)arsenate(V) Sesquihydrate, $(-)_{589}$-K[As(cat)$_3$].1·5H$_2$O

By A. Kobayashi, T. Ito,* F. Marumo and Y. Saito

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

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The crystal structure of potassium $(-)_{589}$-tris(1,2-benzenediolato)arsenate(V) sesquihydrate, $(-)_{589}$-K[As(cat)$_3$].1·5H$_2$O, has been determined from three-dimensional data collected by a diffractometer. The crystals are orthorhombic with space group $P2_12_12_1$: $a=12{\cdot}901$, $b=24{\cdot}852$, $c=11{\cdot}888$ Å and $Z=8$. The structure was refined to an R value of 0·055 for the 1428 observed reflexions. The complex anion has an approximate symmetry D_3. Each ligand molecule is coordinated to the central arsenic atom by their oxygen atoms with the average As–O distance of 1·84 Å. All the bond distances and angles are normal. The absolute configuration of the complex anion was determined by the absorption edge technique. It can be designated as Δ, in accordance with a spectroscopic assignment based on the circular dichroism spectra.

Introduction

The absolute configuration of an optically active metal complex can be determined by means of X-rays (Bijvoet, Peerdeman & van Bommel, 1951). It can also be determined non-empirically by the study of its circular dichroism (CD) associated with transitions localized principally on the ligands. Two or more electric-dipole-allowed transitions are able to couple to yield component transitions which are intrinsically optically active and which have Cotton effects whose signs are determined by the phase relationships of the individual dipoles (Bosnich, 1969). The two methods should give the same result for one particular complex. The absolute configuration of $(-)_{589}$-tris(1,2-benzenediolato)arsenate(V) ion has been studied by X-ray diffraction methods and by the analysis of the CD spectrum to verify that both methods give an identical conclusion. The crystal structure of potassium $(-)_{589}$-tris(1,2-benzenediolato)arsenate(V) sesquihydrate, $(-)_{589}$-K[As(cat)$_3$].1·5H$_2$O is described in this paper.

Experimental

The crystals were prepared according to the method described by Ryschkewitsch & Garrett (1968). They

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* Present address: Department of Chemistry, Faculty of Education, Fukushima University, Hamadacho, Fukushima 960, Japan.

are colourless prismatic crystals elongated along [101]. Oscillation and Weissenberg photographs were taken to determine the cell dimensions and the space group using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å).

The crystal data are: $(-)_{589}$-$C_{18}H_{12}O_6AsK.1{\cdot}5H_2O$, F.W. 465; orthorhombic, $a = 12{\cdot}901$ (2), $b = 24{\cdot}852$ (3), $c = 11{\cdot}888$ (2) Å, $U = 3812$ Å^3; $D_m = 1{\cdot}635$ g.cm^{-3}, $Z = 8$, $D_x = 1{\cdot}622$ g.cm^{-3}.

Space group $P2_12_12_1(D_2^4$, No. 19); linear absorption coefficient for Mo $K\alpha$, $\mu = 22{\cdot}5$ cm^{-1}.

The intensities of reflexions were measured on a Rigaku automated four-circle diffractometer. The crystal used for this purpose had the dimensions $0{\cdot}11 \times 0{\cdot}08 \times 0{\cdot}07$ mm. It was mounted with [101] parallel to the φ axis of the diffractometer. The ω–2θ scan technique was employed. Scan range was calculated from the expression $0{\cdot}8° + 0{\cdot}4° \tan\theta$. Scan speed was 0·5° per min in ω and background counts of 10 sec duration were taken at both limits of the scan. Mo $K\alpha$ radiation monochromated by a LiF crystal was used. A set of standard reflexions was measured every fifty reflexions during the data collection to check the electronic stability of the instrument and to check any deterioration of the crystal. The fluctuations in the intensities of the standard reflexions were within 2–3 %. 4500 intensities were measured up to $2\theta = 55°$, and 1428 of these were more than 3σ over the background, where σ is given by $|F|/2I_o\{I_p - (B_1 + B_2)(T_p/2T_B)^2\}^{1/2}$. I_p and I_o are the total intensity and the net intensity respectively. Both B_1 and B_2 are background counts and T_p and T_B are the times required for the measurements of peak and background intensities respectively. The intensities were corrected for Lorentz and polarization factors, but corrections for absorption and extinction were not made.

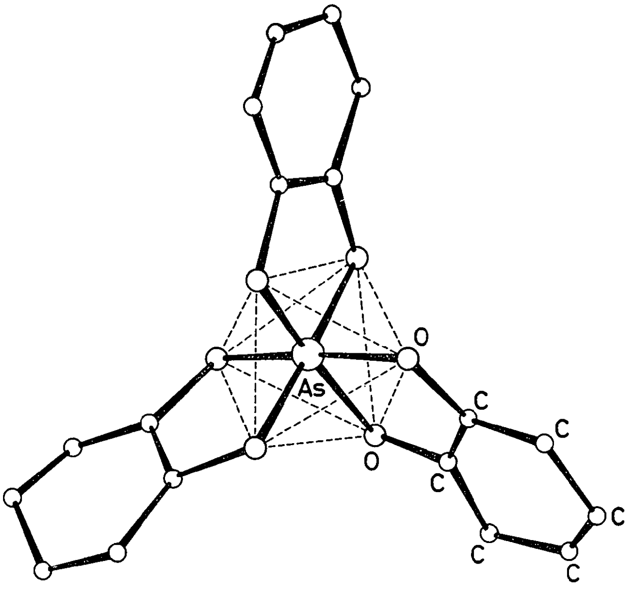

Fig. 1. A perspective drawing of the complex ion $(-)_{589}$-$[As(cat)_3]^-$, viewed along the c axis.

Table 1. *Determination of the absolute configuration*

h	k	l	$\lvert F_{calc}\rvert^2$	Obs	h	k	l	$\lvert F_{calc}\rvert^2$
1	7	1	2884	>	1	7	$\bar{1}$	2841
1	8	1	5898	>	1	8	$\bar{1}$	3745
1	9	1	6288	>	1	9	$\bar{1}$	5461
1	1	4	1467	<	1	$\bar{1}$	4	2061
1	3	3	1296	>	1	$\bar{3}$	3	1050

Table 2. *Final positional parameters with their standard deviations in parentheses* ($\times 10^4$)

	x	y	z
As(1)	5009 (4)	2561 (1)	9417 (2)
As(2)	2537 (3)	4248 (1)	5005 (4)
K(1)	7389 (9)	1811 (2)	9699 (6)
K(2)	1980 (6)	4542 (3)	8084 (7)
O(1)	5227 (16)	2122 (7)	10627 (18)
O(2)	4583 (12)	3097 (7)	10413 (15)
O(3)	3643 (11)	2354 (6)	9209 (14)
O(4)	6339 (11)	2816 (7)	9549 (16)
O(5)	4760 (14)	3054 (7)	8307 (18)
O(6)	5360 (12)	2010 (7)	8423 (16)
O(7)	1415 (15)	4203 (8)	5951 (17)
O(8)	3644 (13)	4356 (7)	4023 (14)
O(9)	2026 (16)	3760 (7)	3996 (18)
O(10)	1832 (11)	4771 (6)	4242 (14)
O(11)	3141 (12)	3683 (7)	5755 (15)
O(12)	3137 (15)	4725 (8)	5996 (17)
C(1)	6517 (19)	3173 (10)	8728 (23)
C(2)	5668 (25)	3327 (10)	8145 (37)
C(3)	5850 (23)	3731 (12)	7315 (26)
C(4)	6761 (23)	4023 (13)	7333 (29)
C(5)	7595 (24)	3849 (10)	7919 (27)
C(6)	7460 (27)	3444 (10)	8715 (22)
C(7)	3587 (23)	1918 (11)	8509 (24)
C(8)	4504 (22)	1708 (12)	8146 (31)
C(9)	4633 (21)	1347 (12)	7257 (22)
C(10)	3759 (22)	1085 (11)	6924 (27)
C(11)	2784 (20)	1279 (11)	7309 (23)
C(12)	2680 (17)	1697 (10)	8069 (20)
C(13)	4871 (19)	2964 (9)	11492 (24)
C(14)	5226 (22)	2431 (16)	11542 (26)
C(15)	5498 (21)	2238 (12)	12597 (26)
C(16)	5481 (23)	2574 (12)	13561 (27)
C(17)	5102 (27)	3097 (13)	13464 (26)
C(18)	4813 (19)	3304 (12)	12444 (30)
C(19)	2330 (20)	3237 (10)	4301 (23)
C(20)	2980 (21)	3206 (10)	5216 (28)
C(21)	3363 (19)	2729 (9)	5616 (25)
C(22)	3134 (25)	2267 (11)	5013 (30)
C(23)	2463 (29)	2293 (11)	4092 (26)
C(24)	2115 (21)	2779 (11)	3693 (27)
C(25)	894 (18)	4882 (10)	4744 (19)
C(26)	682 (25)	4568 (16)	5730 (36)
C(27)	−259 (20)	4672 (12)	6283 (25)
C(28)	−954 (24)	5057 (13)	5873 (28)
C(29)	−737 (27)	5359 (14)	4948 (30)
C(30)	202 (23)	5255 (10)	4385 (26)
C(31)	4387 (18)	4635 (10)	4555 (27)
C(32)	4095 (22)	4837 (11)	5631 (26)
C(33)	4791 (25)	5120 (11)	6307 (24)
C(34)	5794 (24)	5238 (12)	5854 (31)
C(35)	6049 (23)	5005 (13)	4840 (28)
C(36)	5401 (26)	4652 (16)	4246 (34)
O(13)	2502 (19)	4103 (7)	1582 (18)
O(14)	638 (18)	3948 (8)	9309 (20)
O(15)	2962 (16)	3631 (9)	8184 (20)

Determination of the structure

The structure was solved by the heavy-atom method. The density measurement indicated that there are two formula units in the asymmetric unit. Positions of the two arsenic and two potassium atoms were deduced from three-dimensional Patterson maps. One of the arsenic atoms lies close to the twofold screw axis parallel to the *a* axis. The positions of the 12 oxygen atoms in the complex ions were obtained immediately from the three-dimensional Fourier synthesis phased by the heavy atoms. All the carbon atoms and the oxygen atoms of the water molecules were located by successive Fourier syntheses. The atomic coordinates thus obtained were refined by the block-diagonal least-squares method with isotropic temperature factors to an *R* value of 0·12. However, some of the bond distances and bond angles of the complex anion became

Table 3. *Final thermal parameters with their standard deviations in parentheses*

The values have been multiplied by 10^4 and refer to the expression: $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	33 (1)	12 (1)	54 (2)	0 (1)	−1 (4)	−1 (1)
As(2)	48 (2)	16 (0)	61 (2)	−1 (2)	0 (2)	2 (1)
K(1)	49 (5)	17 (1)	117 (9)	5 (3)	−14 (7)	−4 (3)
K(2)	81 (6)	23 (2)	89 (7)	−8 (3)	2 (6)	−13 (3)
O(1)	108 (20)	14 (3)	99 (19)	−18 (8)	32 (20)	−11 (8)
O(2)	54 (14)	22 (4)	52 (18)	−4 (6)	−20 (13)	−18 (7)
O(3)	14 (9)	17 (4)	57 (17)	7 (5)	6 (11)	12 (6)
O(4)	21 (10)	16 (3)	83 (19)	−8 (5)	−22 (13)	10 (7)
O(5)	59 (18)	18 (4)	138 (25)	13 (7)	−20 (17)	−26 (9)
O(6)	29 (13)	23 (5)	80 (20)	7 (6)	18 (13)	1 (8)
O(7)	66 (15)	27 (5)	92 (22)	8 (8)	25 (15)	5 (9)
O(8)	41 (12)	23 (4)	41 (16)	3 (6)	14 (11)	−11 (7)
O(9)	97 (20)	16 (4)	117 (24)	2 (7)	−23 (18)	1 (8)
O(10)	23 (10)	13 (3)	47 (17)	5 (5)	10 (11)	7 (6)
O(11)	28 (11)	18 (4)	52 (17)	11 (6)	−20 (12)	11 (7)
O(12)	76 (18)	24 (5)	87 (21)	−12 (7)	−20 (16)	1 (8)
C(1)	38(20)	12 (6)	61 (27)	4 (9)	−18 (20)	3 (10)
C(2)	102 (29)	7 (6)	99 (34)	16 (11)	19 (28)	3 (11)
C(3)	76 (26)	24 (7)	70 (31)	12 (13)	−45 (25)	4 (13)
C(4)	63 (25)	26 (8)	115 (40)	8 (12)	37 (27)	0 (14)
C(5)	44 (22)	17 (6)	137 (36)	−5 (12)	−15 (28)	−4 (13)
C(6)	91 (26)	14 (6)	65 (26)	−14 (13)	5 (29)	−1 (10)
C(7)	69 (24)	14 (6)	61 (28)	2 (11)	3 (23)	−1 (11)
C(8)	49 (23)	15 (7)	157 (43)	8 (10)	0 (26)	12 (14)
C(9)	68 (26)	23 (7)	32 (26)	−2 (11)	−12 (19)	−13 (11)
C(10)	52 (23)	16 (6)	103 (34)	−3 (11)	−6 (25)	−14 (12)
C(11)	43 (21)	20 (6)	59 (26)	9 (10)	−6 (20)	15 (11)
C(12)	7 (17)	19 (6)	52 (23)	18 (8)	9 (17)	−4 (10)
C(13)	10 (17)	11 (5)	110 (30)	2 (8)	−35 (21)	0 (10)
C(14)	42 (33)	48 (11)	87 (29)	−14 (16)	27 (21)	23 (19)
C(15)	76 (24)	25 (7)	71 (29)	−34 (11)	49 (24)	3 (12)
C(16)	84 (27)	14 (7)	118 (34)	1 (12)	22 (24)	2 (14)
C(17)	84 (28)	32 (8)	93 (33)	−1 (15)	78 (31)	−12 (13)
C(18)	12 (22)	23 (7)	151 (38)	−9 (10)	−3 (25)	−6 (13)
C(19)	47 (20)	14 (5)	66 (24)	−3 (9)	23 (24)	8 (10)
C(20)	77 (24)	6 (5)	140 (42)	−1 (9)	28 (28)	−1 (12)
C(21)	62 (20)	7 (5)	62 (24)	7 (8)	10 (22)	11 (10)
C(22)	121 (29)	18 (7)	99 (31)	−17 (12)	36 (32)	−13 (15)
C(23)	113 (28)	12 (5)	126 (36)	−10 (13)	−20 (34)	−3 (12)
C(24)	62 (26)	13 (6)	111 (34)	−9 (10)	−31 (24)	−4 (12)
C(25)	31 (17)	16 (6)	33 (27)	5 (8)	−10 (16)	−4 (9)
C(26)	69 (26)	35 (10)	178 (49)	−2 (14)	13 (35)	14 (20)
C(27)	41 (25)	26 (8)	78 (28)	−2 (11)	19 (20)	−26 (12)
C(28)	79 (28)	23 (7)	118 (41)	21 (13)	29 (28)	5 (14)
C(29)	112 (30)	32 (9)	113 (36)	13 (14)	51 (36)	21 (17)
C(30)	85 (29)	14 (5)	82 (26)	−12 (10)	−32 (28)	17 (12)
C(31)	31 (17)	12 (6)	115 (32)	16 (8)	−47 (22)	−16 (12)
C(32)	77 (25)	21 (7)	57 (25)	−14 (11)	8 (25)	−18 (13)
C(33)	80 (31)	19 (7)	71 (27)	−8 (12)	−13 (24)	−0 (11)
C(34)	61 (24)	17 (7)	166 (48)	−17 (10)	19 (30)	−16 (15)
C(35)	90 (29)	28 (8)	89 (35)	−15 (13)	3 (28)	18 (14)
C(36)	91 (33)	41 (11)	156 (48)	−24 (15)	51 (33)	4 (19)
O(13)	85 (16)	19 (5)	134 (23)	−7 (10)	7 (21)	11 (8)
O(14)	141 (21)	14 (4)	113 (23)	−2 (8)	58 (22)	−1 (9)
O(15)	68 (18)	33 (6)	119 (25)	25 (8)	−1 (18)	−0 (10)

Table 4. *Observed and calculated structure amplitudes*

H	K	L	FO	FC
2	0	0	11	9
4	0	0	308	308
6	0	0	14	16
8	0	0	133	135
10	0	0	40	20
12	0	0	72	65
1	1	0	281	272
3	1	0	190	184
4	1	0	69	62
5	1	0	97	98
9	1	0	27	25
15	1	0	25	22
0	2	0	120	118
1	2	0	46	29
2	2	0	173	174
3	2	0	41	38
4	2	0	190	187
6	2	0	103	107
7	2	0	51	48
8	2	0	120	118
11	2	0	43	41
14	2	0	39	31
1	3	0	50	62
2	3	0	32	31
4	3	0	51	50
5	3	0	78	93
6	3	0	40	24
10	3	0	39	48
11	3	0	28	28
13	3	0	40	20
0	4	0	248	238
1	4	0	85	81
2	4	0	344	338
5	4	0	49	45
6	4	0	155	157
7	4	0	52	52
8	4	0	38	40
10	4	0	84	80
11	4	0	57	58
14	4	0	42	41
15	4	0	26	30
1	5	0	56	51
2	5	0	48	50
3	5	0	30	36
5	5	0	68	65
6	5	0	98	100
7	5	0	101	101
8	5	0	17	13
11	5	0	36	46
0	6	0	49	44
1	6	0	58	57
2	6	0	34	34
3	6	0	103	99
4	6	0	68	66
6	6	0	64	57
7	6	0	68	68
8	6	0	136	135
12	6	0	50	49
1	7	0	147	139
4	7	0	103	107
5	7	0	164	174
7	7	0	69	72
8	7	0	42	44
9	7	0	67	87
11	7	0	40	42
13	7	0	48	31
1	8	0	37	29
2	8	0	168	167
4	8	0	62	59
5	8	0	60	55
6	8	0	119	117
8	8	0	41	24
9	8	0	40	31
10	8	0	126	126
14	8	0	45	36
1	9	0	132	127
3	9	0	85	94
4	9	0	36	29
6	9	0	15	14
7	9	0	43	87
9	9	0	36	38
4	10	0	65	69
6	10	0	72	69
7	10	0	21	21
10	10	0	47	51
12	10	0	22	20
1	11	0	45	39
2	11	0	16	21
3	11	0	57	50
4	11	0	15	11
5	11	0	108	112
7	11	0	90	86
9	11	0	87	91
11	11	0	29	27
13	11	0	40	23
0	12	0	68	66
1	12	0	26	20
4	12	0	101	105
6	12	0	41	43
8	12	0	143	143
9	12	0	32	34
12	12	0	66	67
3	13	0	48	47
7	13	0	68	67
9	13	0	49	45
11	13	0	38	27
0	14	0	93	90
2	14	0	95	101
4	14	0	58	58
5	14	0	43	44
6	14	0	74	75
10	14	0	47	42
1	15	0	60	56
4	15	0	19	18
5	15	0	34	43
7	15	0	20	16
9	15	0	48	48
0	16	0	79	81
3	16	0	57	63
4	16	0	71	69
7	16	0	60	57
8	16	0	68	69
12	16	0	29	25
1	17	0	21	17
2	17	0	34	31
3	17	0	32	25
6	17	0	26	28
0	18	0	75	70
1	18	0	48	47
2	18	0	38	41
4	18	0	83	83
5	18	0	37	34
7	18	0	24	29
11	18	0	42	33
12	18	0	31	28
1	19	0	73	78
3	19	0	81	76
5	19	0	24	32
7	19	0	47	43
9	19	0	20	22
13	19	0	25	26
0	20	0	64	63
1	20	0	47	49
2	20	0	113	115
3	20	0	47	48
5	20	0	46	45
6	20	0	57	56
10	20	0	42	51
11	20	0	25	25
1	21	0	41	27
9	21	0	26	20
9	22	0	23	24
3	23	0	27	27
9	24	0	33	29
2	25	0	23	20
1	26	0	24	24
2	26	0	35	40
3	26	0	33	38
6	26	0	25	26
1	27	0	21	22
3	27	0	22	18
5	27	0	30	30
0	28	0	28	25
1	0	1	87	89
2	0	1	58	61
3	0	1	101	93
4	0	1	90	95
5	0	1	46	42
0	1	1	165	156
2	1	1	264	266
3	1	1	69	70
4	1	1	111	105
5	1	1	18	23
6	1	1	90	90
7	1	1	45	48
8	1	1	100	102
10	1	1	33	33
12	1	1	30	28
1	2	1	177	180
2	2	1	47	47
3	2	1	112	107
4	2	1	61	52
5	2	1	50	51
7	2	1	58	56
9	2	1	24	29
11	2	1	38	44
15	2	1	20	18
0	3	1	329	345
2	3	1	94	95
3	3	1	27	32
4	3	1	166	162
6	3	1	58	54
8	3	1	162	163
9	3	1	28	24
12	3	1	56	57
0	4	1	112	105
1	4	1	147	146
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4	15	5	56	52
5	15	5	52	54
6	15	5	56	52
1	16	5	63	61
2	16	5	38	30
3	16	5	60	69
5	16	5	50	45
7	16	5	42	33
0	17	5	49	55
2	17	5	32	31
4	17	5	44	49
8	17	5	30	28
12	17	5	24	22
3	18	5	54	67
5	18	5	38	46
7	18	5	48	25
5	20	5	30	26
11	21	5	19	15
3	22	5	31	32
5	22	5	29	27
0	24	5	22	18
2	0	6	115	115
4	0	6	93	89
6	0	6	108	114
7	0	6	38	25
8	0	6	36	35
10	0	6	49	47
14	0	6	48	39
0	1	6	76	72
1	1	6	52	53
3	1	6	111	114
5	1	6	102	102
7	1	6	70	68
9	1	6	68	73
10	1	6	26	21
11	1	6	38	35
13	1	6	42	40
1	2	6	64	60
2	2	6	37	27
3	2	6	37	31
4	2	6	66	55
6	2	6	15	15
8	2	6	65	66
12	2	6	29	34
0	3	6	91	92
1	3	6	81	83
2	3	6	47	43
5	3	6	57	57
7	3	6	50	49
9	3	6	52	58
0	4	6	68	68
1	4	6	18	13
4	4	6	69	65
7	4	6	19	20
8	4	6	63	60
12	4	6	25	26
1	5	6	84	85
2	5	6	62	60
3	5	6	95	98
5	5	6	53	48
6	5	6	44	44
7	5	6	62	61
10	5	6	30	28
13	5	6	28	26
2	6	6	117	117
4	6	6	35	49
6	6	6	90	84
10	6	6	41	36
14	6	6	44	40
1	7	6	101	102
2	7	6	25	20
3	7	6	106	103
5	7	6	89	94
6	7	6	23	20
7	7	6	63	65
9	7	6	45	49
0	8	6	176	178
1	8	6	14	16
4	8	6	109	113
7	8	6	23	18
8	8	6	52	48
12	8	6	36	33
0	9	6	64	67
1	9	6	65	67
2	9	6	39	38
3	9	6	67	66
7	9	6	50	50
8	9	6	46	49
0	10	6	51	45
2	10	6	43	44
4	10	6	38	34
6	10	6	38	49
8	10	6	46	48
0	11	6	65	59
1	11	6	68	70
3	11	6	58	65
4	11	6	48	46
5	11	6	40	44
7	11	6	29	29
0	12	6	36	31
1	12	6	17	15
2	12	6	80	78
4	12	6	43	40
6	12	6	78	80
11	12	6	27	23
1	13	6	69	68
2	13	6	26	31
3	13	6	68	66
5	13	6	50	60
7	13	6	51	50
8	13	6	20	25
9	13	6	34	37
0	14	6	50	50
3	14	6	44	44
4	14	6	54	62
3	15	6	52	53
5	15	6	60	63
1	16	6	48	29
5	16	6	42	49
2	17	6	42	22
7	17	6	44	25
9	17	6	46	28
10	17	6	42	20
11	17	6	41	20
3	18	6	27	27
6	18	6	30	27
1	19	6	29	31
3	19	6	32	32
4	19	6	41	21
5	19	6	42	41
4	20	6	42	40
6	20	6	31	27
5	21	6	30	28
7	21	6	38	36
11	21	6	24	24
6	22	6	21	27
1	0	7	53	57
3	0	7	42	44
7	0	7	52	53
0	1	7	59	56
2	1	7	38	41
4	1	7	72	75
6	1	7	41	35
8	1	7	55	57
10	1	7	22	21
1	2	7	58	59
3	2	7	42	35
5	2	7	73	76
6	2	7	26	32
7	2	7	37	37
8	2	7	27	26
9	2	7	37	27
0	3	7	33	31
2	3	7	109	105
4	3	7	42	42
6	3	7	102	105
10	3	7	56	57
14	3	7	33	35
1	4	7	80	77
2	4	7	36	32
3	4	7	75	75
5	4	7	72	69
9	4	7	40	39
11	4	7	27	28
0	5	7	128	129
1	5	7	19	21
3	5	7	24	25
4	5	7	93	94
8	5	7	72	69
12	5	7	29	31
1	6	7	29	29
3	6	7	58	54
5	6	7	16	14
6	6	7	28	33
7	6	7	56	58
0	7	7	72	76
2	7	7	36	43
4	7	7	43	41
5	7	7	26	24
8	7	7	47	45
1	8	7	30	31
3	8	7	48	48
5	8	7	42	40
7	8	7	38	33
2	9	7	85	87
5	9	7	19	23
6	9	7	76	78
10	9	7	46	42
14	9	7	43	36
0	10	7	49	51
1	10	7	60	64
3	10	7	52	53
5	10	7	24	22
9	10	7	26	25
0	11	7	102	100
1	11	7	16	16
3	11	7	37	45
4	11	7	64	69
8	11	7	36	48
0	12	7	67	69
1	12	7	46	49
2	12	7	19	17
3	12	7	50	54
4	12	7	38	40
5	12	7	61	67
6	12	7	21	20
9	12	7	23	22
13	12	7	23	26
1	13	7	40	39
2	13	7	60	69
3	13	7	30	35
4	13	7	26	26
5	13	7	22	21
6	13	7	28	29
10	13	7	22	24
2	14	7	45	43
3	14	7	48	50
2	15	7	54	56
6	15	7	44	45
7	15	7	20	22
10	15	7	33	34
11	15	7	19	24
1	16	7	38	33
3	16	7	42	32
5	16	7	43	42
6	16	7	20	22
7	16	7	38	32
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1	17	7	27	32
4	17	7	49	50
5	17	7	21	26
8	17	7	41	42
12	17	7	26	26
1	18	7	21	25
5	19	7	36	36
6	19	7	32	28
10	19	7	22	27
6	20	7	22	19
2	21	7	23	25
4	23	7	33	32
2	25	7	24	19
0	0	8	63	59
1	0	8	47	47
2	0	8	105	98
6	0	8	95	95
9	0	8	21	22
10	0	8	58	60
1	1	8	40	29
3	1	8	46	48
4	1	8	30	35
5	1	8	50	45
7	1	8	55	58
9	1	8	41	46
0	2	8	79	82
2	2	8	50	48
4	2	8	77	79
5	2	8	19	15
6	2	8	37	31
8	2	8	81	84
0	3	8	39	41
6	3	8	35	34
7	3	8	29	25
0	4	8	81	81
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5	4	8	23	24
6	4	8	42	41
8	4	8	48	50
1	5	8	41	46
3	5	8	37	37
6	5	8	29	27
7	5	8	24	22
13	5	8	22	20
2	6	8	97	102
6	6	8	85	89
10	6	8	42	50
1	7	8	57	60
3	7	8	53	53
7	7	8	39	39
0	8	8	81	81
1	8	8	25	24
3	8	8	26	31
4	8	8	44	52
5	8	8	39	41
6	8	8	25	27
8	8	8	58	64
12	8	8	45	39
0	9	8	38	39
5	9	8	31	31
0	10	8	48	55
2	10	8	26	30
4	10	8	45	44
5	10	8	44	44
7	10	8	17	18
1	11	8	37	40
3	11	8	51	49
1	12	8	23	22
2	12	8	78	78
6	12	8	43	40
10	12	8	32	33
0	13	8	47	44
1	13	8	53	52
3	13	8	19	19
0	14	8	83	87
4	14	8	65	69
8	14	8	41	40
12	14	8	27	25
0	15	8	23	18
2	15	8	18	14
1	18	8	33	35
2	18	8	40	44
3	18	8	22	22
6	18	8	36	38
1	19	8	25	24
7	19	8	21	21
0	20	8	45	42
1	20	8	23	23
4	20	8	42	42
1	21	8	33	32
0	26	8	24	24
4	0	9	16	10
0	1	9	124	128
4	1	9	71	75
6	1	9	24	25
8	1	9	48	45
0	2	9	28	30
1	2	9	60	59
3	2	9	46	44
9	2	9	30	32
6	3	9	75	74
10	3	9	49	46
1	4	9	63	63
3	4	9	53	50
7	4	9	52	44
0	5	9	94	91
3	5	9	18	16
4	5	9	72	71
6	5	9	43	37
8	5	9	62	70
12	5	9	41	32
5	6	9	26	26
0	7	9	71	65
1	7	9	22	23
4	7	9	49	50
5	7	9	42	39
8	7	9	31	33
10	7	9	21	24
1	8	9	26	27
2	8	9	18	18
3	8	9	43	41
4	8	9	17	18
5	8	9	49	48
2	9	9	72	72
3	9	9	17	18
4	9	9	24	22
6	9	9	62	65
10	9	9	40	51
1	10	9	54	59
5	10	9	21	22
9	10	9	29	31
0	11	9	57	57
4	11	9	43	47
12	11	9	34	30
2	15	9	67	43
5	15	9	24	24
6	15	9	35	35
1	16	9	28	28
0	17	9	59	55
4	17	9	47	54
6	19	9	27	28
2	21	9	32	28
2	0	10	123	123
6	0	10	61	64
9	0	10	22	22
10	0	10	40	30
1	1	10	60	59
3	1	10	61	59
4	1	10	20	20
0	2	10	109	111
2	2	10	20	23
4	2	10	52	56
8	2	10	39	44
12	2	10	24	22
6	3	10	30	30
0	4	10	63	62
2	4	10	38	41
4	4	10	48	51
6	4	10	25	28
1	5	10	45	40
4	5	10	44	41
5	5	10	41	46
9	5	10	26	27
1	6	10	21	23
2	6	10	72	73
6	6	10	50	51
10	6	10	37	42
1	7	10	50	44
3	7	10	27	25
7	7	10	45	41
0	8	10	63	58
4	8	10	46	45
7	8	10	23	22
8	8	10	34	38
1	10	10	17	19
2	10	10	36	35
4	10	10	27	22
6	10	10	20	21
1	11	10	21	24
6	12	10	49	42
10	12	10	39	39
5	13	10	36	31
9	13	10	29	25
4	14	10	38	40
0	15	10	16	15
1	15	10	38	30
2	16	10	27	27
1	17	10	24	21
2	19	10	17	13
0	20	10	36	37
7	0	11	23	24
1	2	11	39	43
3	2	11	28	30
4	2	11	19	19
9	2	11	22	25
2	3	11	58	56
10	3	11	36	35
1	4	11	51	46
7	4	11	38	36
0	5	11	48	45
7	6	11	27	24
9	6	11	29	27
4	7	11	25	24
0	9	11	30	29
6	9	11	43	43
10	9	11	33	35
1	10	11	43	39
3	10	11	30	28
7	10	11	32	30
9	10	11	27	27
0	11	11	35	32
4	11	11	31	33
8	11	11	28	31
6	12	11	25	27
4	13	11	20	18
2	15	11	25	27
1	16	11	33	31
0	17	11	35	37
4	17	11	29	24
1	18	11	31	30
2	0	12	36	34
1	1	12	43	39
3	1	12	34	39
5	1	12	20	23
1	5	12	36	46
5	5	12	43	38
0	6	12	30	30
2	6	12	32	35
6	6	12	33	29
3	7	12	35	27
7	7	12	26	26
9	7	12	28	30
0	8	12	24	19
4	8	12	26	24
8	8	12	25	25
1	9	12	28	27
9	9	12	20	17
2	12	12	24	21
3	13	12	37	29
7	13	12	29	27
5	15	12	24	21
1	0	13	31	29
4	2	13	29	29
0	3	13	53	33
2	3	13	25	23
1	4	13	38	34
3	4	13	29	27
5	4	13	37	28
5	8	13	21	24
7	8	13	20	22
4	11	13	19	17
6	11	13	24	20
1	12	13	27	25
4	0	14	36	23
4	6	14	24	22
3	9	14	24	22
2	5	15	23	19

absurd. Patterson maps were then re-examined more closely. It turned out that one of the potassium atoms was incorrectly located. After this atom was moved to the correct position, the R value was reduced to 0·09 by four cycles of further refinement.

By means of a difference synthesis all the hydrogen atoms could be located; however, the positions of some of them were adjusted by the calculation of interatomic distances and bond angles. Further cycles of refinement were carried out with the use of anisotropic temperature factors for all the atoms except hydrogen. 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. The absolute configuration of the complex ion was determined by using the absorption edge technique. An equi-inclination Weissenberg photograph was taken of the first layer line about the a axis with Cr $K\alpha$ radiation ($\lambda = 2{\cdot}2909$ Å, $\Delta f' = -0{\cdot}7$, $\Delta f'' = 2{\cdot}2$ for As). Some of the calculated intensities and the observed relations between a reflexion and its counter reflexion are compared in Table 1. From Table 1, it may be concluded that the complex anion illustrated in Fig. 1 corresponds to the laevorotatory form with respect to the Na D lines. The absolute configuration can be designated as Δ according to the IUPAC (1968) convention. The final R value was 0·055 for 1428 observed reflexions. A weighting scheme, $w = 1$ if $|F_o| \geq 10{\cdot}0$, otherwise $w = 0{\cdot}2$, was employed. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final positional parameters and temperature factors are listed in Tables 2 and 3 together with their estimated standard deviations. The calculated and observed structure amplitudes are compared in Table 4.

Description of the structure and discussion

A perspective drawing of the complex ion, $(-)_{589}$-$[As(cat)_3]^-$ is presented in Fig. 1. It correctly represents its absolute configuration. The interatomic distances and bond angles within the complex ions are listed in Table 5. The crystal structure projected along the *c* axis is shown in Fig. 2. The complex ion has a tris-chelate structure and not the bis-chelate structure with a monodentate ligand previously reported (Reilen, Sapper & Kall, 1925; Craddock & Jones, 1961). Both of the two crystallographically independent complex ions show similar shape and size. The complex ion has an approximate symmetry D_3. Each ligand molecule is coordinated to the central arsenic atom by its oxygen atoms with average As–O distance of 1·84 Å. The six oxygen atoms form a distorted octahedron around the arsenic atom. The O–C distances average to 1·39 Å. The OAsO angles in the chelate rings are all less than 90°, the average being 87·0 (9)°. The average AsOC angle is 110°. The angles OCC in the chelate rings are slightly compressed to 115° on average owing to the ring formation. The displacements of oxygen atoms from the regular octahedral position is small. The upper face of an octahedron formed by the three oxygen atoms is rotated clockwise about the threefold axis of D_3 by about 5° with respect to the triangle of the three remaining oxygen atoms from the position expected for a regular octahedron. The distance between the two triangles is 2·17 Å.

Table 5. *Interatomic distances and bond angles within the complex ion*

As(1)–O(1)	1·83 (2) Å	As(2)–O(7)	1·84 (2) Å
As(1)–O(2)	1·86 (2)	As(2)–O(8)	1·86 (2)
As(1)–O(3)	1·85 (1)	As(2)–O(9)	1·83 (2)
As(1)–O(4)	1·84 (1)	As(2)–O(10)	1·83 (1)
As(1)–O(5)	1·83 (2)	As(2)–O(11)	1·84 (2)
As(1)–O(6)	1·87 (2)	As(2)–O(12)	1·84 (2)
O(1)—C(14)	1·33 (4)	O(7)—C(26)	1·34 (4)
O(2)—C(13)	1·38 (3)	O(8)—C(31)	1·34 (3)
O(3)—C(7)	1·37 (3)	O(9)—C(19)	1·41 (3)
O(4)—C(1)	1·34 (3)	O(10)–C(25)	1·38 (3)
O(5)—C(2)	1·37 (3)	O(11)–C(20)	1·36 (3)
O(6)—C(8)	1·37 (3)	O(12)–C(32)	1·34 (3)
C(1)—C(2)	1·35 (4)	C(7)—C(8)	1·36 (4)
C(2)—C(3)	1·43 (4)	C(8)—C(9)	1·40 (4)
C(3)—C(4)	1·38 (4)	C(9)—C(10)	1·36 (4)
C(4)—C(5)	1·35 (4)	C(10)–C(11)	1·42 (4)
C(5)—C(6)	1·39 (4)	C(11)–C(12)	1·38 (3)
C(6)—C(1)	1·39 (4)	C(12)–C(7)	1·39 (3)
C(13)–C(14)	1·40 (4)	C(19)–C(20)	1·38 (4)
C(14)–C(15)	1·39 (4)	C(20)–C(21)	1·37 (3)
C(15)–C(16)	1·42 (4)	C(21)–C(22)	1·39 (4)
C(16)–C(17)	1·39 (4)	C(22)–C(23)	1·40 (4)
C(17)–C(18)	1·37 (4)	C(23)–C(24)	1·37 (4)
C(18)–C(13)	1·41 (4)	C(24)–C(19)	1·38 (4)
C(25)–C(26)	1·43 (4)	C(31)–C(32)	1·43 (4)
C(26)–C(27)	1·40 (4)	C(32)–C(33)	1·40 (4)
C(27)–C(28)	1·40 (4)	C(33)–C(34)	1·43 (4)
C(28)–C(29)	1·36 (4)	C(34)–C(35)	1·38 (4)
C(29)–C(30)	1·41 (4)	C(35)–C(36)	1·40 (5)
C(30)–C(25)	1·36 (3)	C(36)–C(31)	1·36 (4)

Table 5 (*cont.*)

O(1)—As(1)–O(2)	88·4 (0·6)°	O(7)—As(2)–O(10)	87·4 (0·7)°
O(3)—As(1)–O(6)	86·6 (0·5)	O(9)—As(2)–O(11)	87·9 (0·6)
O(4)—As(1)–O(5)	89·8 (0·6)	O(8)—As(2)–O(12)	89·2 (0·7)
As(1)–O(4)—C(1)	109·0 (1·2)	As(2)—O(7)–C(26)	113·3 (1·4)
As(1)–O(5)—C(2)	106·4 (1·5)	As(2)–O(8)—C(31)	109·1 (1·3)
As(1)–O(3)—C(7)	110·6 (1·0)	As(2)–O(9)—C(19)	110·1 (1·2)
As(1)–O(6)—C(8)	111·0 (1·3)	As(2)–O(10)–C(25)	111·4 (1·1)
As(1)–O(1)—C(14)	107·3 (1·0)	As(2)–O(11)–C(20)	111·8 (1·1)
As(1)–O(2)—C(13)	109·9 (1·1)	As(2)–O(12)–C(32)	108·4 (1·5)
O(4)—C(1)—C(2)	115·0 (2·0)	O(7)—C(26)–C(25)	113·3 (2·5)
O(5)—C(2)—C(1)	118·8 (1·8)	O(8)—C(31)–C(32)	114·6 (2·0)
O(3)—C(7)—C(8)	116·7 (2·1)	O(9)—C(19)–C(20)	115·2 (1·6)
O(6)—C(8)—C(7)	114·3 (1·7)	O(10)–C(25)–C(26)	114·4 (1·8)
O(1)—C(14)–C(13)	120·7 (2·0)	O(11)–C(20)–C(19)	114·7 (1·5)
O(2)—C(13)–C(14)	110·8 (1·6)	O(12)–C(32)–C(31)	117·4 (2·1)
C(1)—C(2)—C(3)	114·9 (2·2)	C(19)–C(20)–C(21)	122·8 (1·6)
C(2)—C(3)—C(4)	119·9 (2·3)	C(20)–C(21)–C(22)	117·5 (2·1)
C(3)—C(4)—C(5)	121·1 (1·9)	C(21)–C(22)–C(23)	119·8 (1·8)
C(4)—C(5)—C(6)	118·8 (2·3)	C(22)–C(23)–C(24)	121·0 (1·8)
C(5)—C(6)—C(1)	117·9 (2·3)	C(23)–C(24)–C(19)	118·7 (2·2)
C(6)—C(1)—C(2)	124·0 (2·1)	C(24)–C(19)–C(20)	119·5 (1·6)
C(7)—C(8)—C(9)	126·1 (2·3)	C(25)–C(26)–C(27)	116·6 (2·0)
C(8)—C(9)—C(10)	115·5 (2·2)	C(26)–C(27)–C(28)	121·1 (2·3)
C(9)—C(10)–C(11)	118·4 (1·8)	C(27)–C(28)–C(29)	121·8 (2·5)
C(10)–C(11)–C(12)	123·4 (1·9)	C(28)–C(29)–C(30)	117·4 (2·2)
C(11)–C(12)–C(7)	117·4 (1·8)	C(29)–C(30)–C(25)	122·8 (2·3)
C(12)–C(7)—C(8)	117·3 (1·8)	C(30)–C(25)–C(26)	120·3 (2·2)
C(13)–C(14)–C(15)	116·6 (1·9)	C(31)–C(32)–C(33)	121·7 (2·4)
C(14)–C(15)–C(16)	121·5 (1·5)	C(32)–C(33)–C(34)	117·9 (2·3)
C(15)–C(16)–C(17)	119·2 (2·2)	C(33)–C(34)–C(35)	117·3 (2·3)
C(16)–C(17)–C(18)	121·3 (2·2)	C(34)–C(35)–C(36)	124·2 (2·6)
C(17)–C(18)–C(13)	118·0 (1·5)	C(35)–C(36)–C(31)	117·2 (2·5)
C(18)–C(13)–C(14)	123·2 (2·0)	C(36)–C(31)–C(32)	119·0 (2·4)

Two of the three planar ligands in a complex ion, *i.e.* the ligands containing C(1) to C(6), C(7) to C(12) in

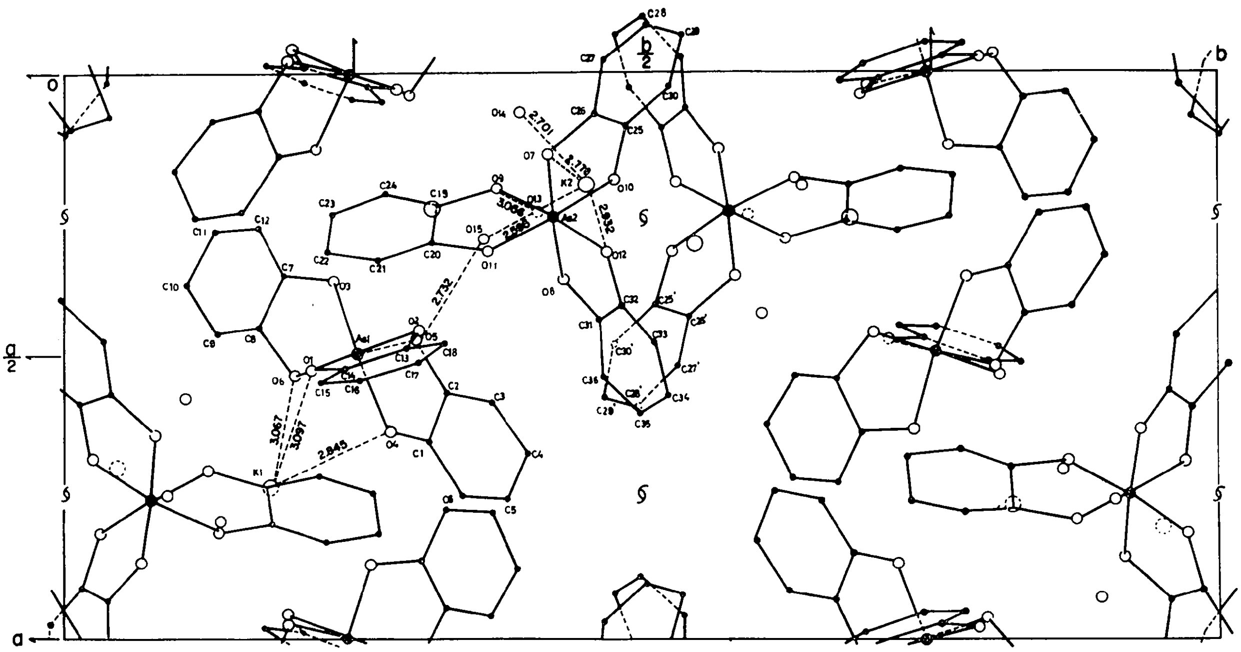

Fig. 2. A projection of the structure along the c-axis. Broken lines indicate some close contacts.

one complex ion and those containing C(19) to C(24), C(25) to C(30) in the other, make an angle of only about 2° with the corresponding coordination planes. However, the remaining ligands, those containing C(13) to C(18) and C(31) to C(36), are inclined by an angle of 12° with the coordination planes. If the plane O–As–O and the benzene ring were coplanar, the distances C(17)···C(20) and C(35)···C(28′) between adjacent complex ions would become as short as 2·8 Å. Accordingly, the observed distortion is certainly due to the packing in the crystal lattice.

The close contacts are observed between the oxygen atom of the complex ion and the potassium ions, and between the oxygen atoms of the complex ions and those of the water molecules. There also exist short contacts between potassium ions and oxygen atoms of the water molecules. They are listed in Table 6 and are also indicated by broken lines in Fig. 2.

Table 6. *Interatomic distances less than* 3·5 Å *outside the complex ions*

K(1)····O(4)	2·85 (2) Å
K(1)····O(6)	3·07 (2)
K(2)····O(12)	2·93 (2)
K(2)····O(14)	2·70 (2)
K(1)····O(1)	3·10 (2)
K(2)····O(7)	2·77 (2)
K(2)····C(26)	3·26 (4)
K(2)····O(15)	2·60 (2)
O(5)····O(15)	2·73 (3)
O(8)····O(13)	3·32 (3)
O(9)····O(13)	3·06 (3)
O(11)···O(15)	2·90 (3)
O(14)···O(15)	3·38 (3)
C(17)···C(20)	3·45 (4)

The circular dichroism spectra of $(-)_{589}$-[As(cat)$_3$]$^-$ in aqueous solution were measured and interpreted satisfactorily in terms of the calculated transition energies and the oscillator strengths (Kunii & Kuroda, 1968). According to the theory of exciton circular dichroism, the observed circular dichroism spectra indicate that the absolute configuration of the complex ion is Δ (Ito, Kobayashi, Marumo & Saito, 1971). Consequently the two methods give the same picture.

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