ACTA CHEMICA SCANDINAVICA **26** (1972) 2349–2359

Walden Inversion

II. The Crystal Structure and Absolute Configuration of Cobalt(II) (—)-Malate Trihydrate

LARS KRYGER and SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Cobalt(II) (–)-malate trihydrate ($Co(OOC-CH_2-CHOH-COO)\cdot 3H_2O$) is monoclinic with $a=8.450$ Å, $b=9.062$ Å, $c=5.789$ Å, and $\beta=105.42°$. The space group is $P2_1$ (No. 4), and there are 2 formula units per unit cell. The X-ray analysis was based on intensity data obtained from an automatic counter diffractometer using Mo$K\alpha$ radiation. The positions of all the atoms were found. The structure was refined to an R-factor of 0.028. The absolute configuration of the (–)-malate group was found by the anomalous dispersion method. The cobalt atoms were excited by Cu$K\alpha$ radiation and a comparison of 20 Friedel related reflections gave an unequivocal indication of the chirality of the (–)-malate group. A discussion is given of the Walden inversion in the chlorosuccinic acid-malic acid reaction.

The inversion of optical activity and hence of chirality in a sequence of reactions was discovered by Walden[1] who was able to convert (–)-malic acid *via* (+)-chlorosuccinic acid to (+)-malic acid. In a Walden cycle some reactions must retain configuration whereas others must invert configuration. The determination of absolute configuration by anomalous scattering of X-rays of two of the species in a Walden cycle appeared to be the obvious method to decide which reaction produces a change in chirality.

This work on the absolute configuration of the (–)-malate group together with a previous paper[2] on the crystal structure and absolute configuration of (–)-chlorosuccinic acid shows that (–)-chlorosuccinic acid and (–)-malic acid have the same chirality. Some correlations with chemical experience are discussed.

EXPERIMENTAL

Chemistry

The cobalt(II) (–)-malate trihydrate was prepared by adding cobalt(II) carbonate to a boiling aqueous solution of (–)-malic acid (mol ratio 1/1). From this solution the compound crystallized at slow cooling in a Dewar flask.

Optical activity

The specific rotation of the malic acid used for the synthesis was checked. Furthermore the specific rotations of cobalt(II) (–)-malate trihydrate and malic acid extracted from the cobalt salt by precipitating cobalt with sodium sulphide were measured: (–)-malic acid, starting product: $\alpha_D^{22} = -1.3°$, uranyl (–)-malic acid complex: $\alpha_D^{22} = -426°$, cobalt(II) (–)-malate trihydrate $\alpha_D = +47°$, extracted malic acid–uranyl complex $\alpha_D = -386°$. Thus malic acid did not undergo an inversion in forming the cobalt complex. A Zeiss Kreis polarimeter equipped with a sodium lamp was used.

X-Ray intensity measurements

(a) Mo$K\alpha$ data (graphite monochromatized radiation). Intensities hkl $l=0$ to 7 were recorded with a linear diffractometer of the Arndt-Phillips design.[3] A pulse height analyzer and a scintillation counter were used. Reflections within a hemisphere of reciprocal space were measured out to a Bragg angle of 30°. Rejecting all reflections for which $\xi < 0.1$ and averaging symmetry related sets, 1101 independent reflections were obtained. Of these 996 had an intensity greater than twice the standard deviation estimated as the square root of the total number of counts in an intensity measurement.

(b) Cu$K\alpha$ data (graphite monochromatized radiation). Again the linear diffractometer was used, equipped for counting as before. The intensities of Friedel pairs $hk0$ and $\bar{h}\bar{k}0$ were recorded out to a Bragg angle of 28°, giving a total of 20 independent pairs.

Table 1. Atomic coordinates, their estimated standard deviations are multiplied by 10^4. The isotropic temperature factor coefficients and their estimated standard deviations (in Å^2) are given for the hydrogen atoms.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Co	0.1685	1	0.0000	–	0.0252	1	–	
O1	0.2752	4	0.0544	4	0.3793	5	–	
O2	0.3979	4	0.0947	3	0.0153	5	–	
O3	0.0804	4	0.2133	3	0.9595	7	–	
O4	0.9275	4	0.9561	3	0.0340	6	–	
O5	0.2450	3	0.7830	3	0.1086	6	–	
O6	0.1123	4	0.9392	4	0.6676	6	–	
O7	0.4532	4	0.2058	4	0.6122	6	–	
O8	0.1463	5	0.6431	4	0.5969	7	–	
C1	0.3850	5	0.1526	5	0.4142	7	–	
C2	0.4309	5	0.2103	5	0.1912	7	–	
C3	0.1496	4	0.3362	4	0.0001	7	–	
C4	0.3353	5	0.3491	4	0.0964	8	–	
H1	0.3750	50	0.3926	50	0.9849	74	1.1	0.9
H2	0.3549	53	0.4219	50	0.2046	86	1.3	0.9
H3	0.1801	67	0.9867	87	0.5598	103	4.3	1.3
H4	0.4645	52	0.7250	51	0.7622	78	1.2	0.9
H5	0.3277	56	0.7775	54	0.2193	93	2.3	1.0
H6	0.4147	56	0.1281	53	0.9112	86	2.0	1.0
H7	0.1407	80	0.6059	78	0.7110	124	5.8	1.7
H8	0.1775	67	0.7484	71	0.1270	112	4.1	1.4
H9	0.0898	81	0.6203	77	0.5171	131	6.2	1.7
H10	0.1108	61	0.8694	60	0.6500	94	2.5	1.1

CRYSTAL DATA

The compound $Co(OOC-CH_2-CHOH-COO).3H_2O$, M = 245, is monoclinic $a = 8.450$ Å, $\sigma(a) = 0.006$ Å. $b = 9.062$ Å, $\sigma(b) = 0.010$ Å. $c = 5.789$ Å, $\sigma(c) = 0.002$ Å. $\beta = 105.42°$, $\sigma(\beta) = 0.04°$. $V_c = 427$ Å^3, density found by flotation in $CCl_4/CHBr_3$: 1.89 g cm^{-3}. Density calculated for $n = 2$: 1.91 g cm^{-3}.

Cu$K\alpha$-radiation was used for single crystal oscillation, Weissenberg and precession photographs. Reflections $0k0$ were absent for $k = 2n + 1$. The crystals are piezoelectric, and hence the space group is $P2_1$ in agreement with the fact that the compound was prepared from optically active malic acid.

Table 2. Thermal parameters (in Å$^2 \times 10^{-4}$) and their estimated standard deviations (in Å$^2 \times 10^{-7}$).

	u_{11}	$\sigma(u_{11})$	u_{22}	$\sigma(u_{22})$	u_{33}	$\sigma(u_{33})$	u_{12}	$\sigma(u_{12})$	u_{13}	$\sigma(u_{13})$	u_{23}	$\sigma(u_{23})$
Co	145	2	142	2	178	2	−3	2	24	2	7	2
O1	308	16	349	18	199	14	−128	15	43	13	−9	15
O2	191	14	200	15	231	14	11	12	96	12	4	12
O3	170	14	136	14	527	21	−23	12	27	15	4	15
O4	196	14	169	15	396	17	−23	14	83	13	−34	15
O5	191	14	212	16	344	17	21	12	10	13	72	14
O6	365	18	234	15	244	15	−48	14	93	14	8	14
O7	282	17	434	22	206	15	−110	16	13	13	−39	15
O8	588	26	391	24	384	20	−185	20	77	19	4	18
C1	144	17	226	20	179	19	−18	15	23	16	7	16
C2	84	16	231	21	236	19	−8	16	25	15	−9	17
C3	107	17	164	21	288	22	3	15	54	17	37	18
C4	116	18	141	20	331	24	−28	15	13	17	5	18

Table 3. Bond lengths in Å and their estimated standard deviations (in Å $\times 10^{-3}$).

	l	$\sigma(l)$		l	$\sigma(l)$
Co−O1	2.067	3	C4−H1	0.879	42
Co−O2	2.136	3	C4−H2	0.911	43
Co−O3	2.071	3	O2−H6	0.808	50
Co−O4	2.088	3	O2−O7	2.691	4
Co−O5	2.086	3	O5−O7	2.721	4
Co−O6	2.073	3	O5−H5	0.868	40
O3−C3	1.251	5	O5−H8	0.763	58
O4−C3	1.257	5	O6−O1	2.646	5
O1−C1	1.262	5	O6−O8	2.732	5
O7−C1	1.237	5	O6−O8	2.960	4
O2−C2	1.435	5	O6−H3	0.982	59
C3−C4	1.521	5	O6−H10	0.842	53
C4−C2	1.517	5	O8−O4	2.921	5
C2−C1	1.534	6	O8−H9	0.718	57
C2−H4	0.862	41	O8−H7	0.825	66

The crystals are dark red and are elongated in the [001] direction and bounded by {110} and {010}. The terminating phaces are irregular. The crystal from which diffractometer data were obtained was 0.5 mm long and the average diameter was approximately 0.05 mm.

The linear absorption coefficients are $\mu = 21.1$ cm^{-1} for Mo*K*α-radiation and $\mu = 156$ cm^{-1} for Cu*K*α-radiation.

Atomic coordinates, thermal parameters, bond lengths and angles, dihedral angles, observed and calculated structure factors and phases are listed in Tables 1 – 6. Fig. 1 shows the coordination octahedra in the structure. Fig. 2 shows the (–)-malate group in its absolute configuration.

Table 4. Angles and their standard deviations (in degrees).

	v°	$\sigma(v)^{\circ}$		v°	$\sigma(v)^{\circ}$
O1 – Co – O2	76.82	0.12	C3 – C4 – H1	108.20	2.19
O1 – Co – O3	90.49	0.12	C3 – C4 – H2	107.89	2.63
O1 – Co – O4	101.02	0.13	H1 – C4 – H2	98.29	3.94
O1 – Co – O5	88.18	0.12	H1 – C4 – C2	111.44	2.57
O1 – Co – O6	167.91	0.13	H2 – C4 – C2	111.51	2.49
O2 – Co – O3	84.36	0.11	C4 – C2 – C1	110.92	0.35
O2 – Co – O4	167.28	0.10	C4 – C2 – O2	111.29	0.29
O2 – Co – O5	99.06	0.11	C4 – C2 – H4	112.26	2.96
O2 – Co – O6	92.81	0.12	O2 – C2 – C1	107.80	0.32
O3 – Co – O4	83.12	0.11	O2 – C2 – H4	107.47	3.06
O3 – Co – O5	175.94	0.14	H4 – C2 – C1	106.87	3.00
O3 – Co – O6	94.71	0.13	C2 – O2 – H6	104.82	3.14
O4 – Co – O5	93.37	0.11	C2 – C1 – O7	119.17	0.34
O4 – Co – O6	90.46	0.13	C2 – C1 – O1	116.44	0.32
O5 – Co – O6	87.34	0.12	O1 – C1 – O7	124.38	0.40
O3 – C3 – O4	122.79	0.32	H5 – O5 – H8	113.85	5.19
O3 – C3 – C4	121.61	0.32	H3 – O6 – H10	108.00	5.67
O4 – C3 – C4	115.58	0.32	H7 – O8 – H9	101.24	6.77
C2 – C4 – C3	117.71	0.32			

Table 5. Dihedral angles in degrees.

Atom sequence	Dihedral angle	Atom sequence	Dihedral angle
Co – O3 – C3 – C4	6.2	O2 – C2 – C1 – O1	– 27.3
O3 – C3 – C4 – C2	– 12.7	C2 – C1 – O1 – Co	– 3.7
C3 – C4 – C2 – C1	– 64.9	C1 – O1 – Co – O2	21.9
C4 – C2 – C1 – O1	94.8	O1 – Co – O2 – C2	– 35.1
C2 – C1 – O1 – Co	– 3.7	C3 – C4 – C2 – O2	55.0
C1 – O1 – Co – O3	– 62.5	C4 – C2 – O2 – Co	– 79.7
O1 – Co – O3 – C3	52.0	C2 – O2 – Co – O3	56.2
Co – O2 – C2 – C1	42.1	O2 – Co – O3 – C3	– 24.7

Table 6.

h	k	l	fobs	fcalc	phase
2	0	0	224	222	183
3	0	0	522	533	182
4	0	0	443	448	181
5	0	0	87	85	7
6	0	0	65	67	15
7	0	0	134	130	3
8	0	0	106	106	185
9	0	0	174	177	185
10	0	0	93	93	183
2	1	0	377	381	26
3	1	0	421	417	181
4	1	0	402	404	-86
5	1	0	188	188	255
7	1	0	96	100	121
8	1	0	193	197	95
9	1	0	60	60	-20
10	1	0	131	131	-73
0	2	0	331	336	43
1	2	0	504	520	-32
2	2	0	311	310	160
3	2	0	281	283	191
4	2	0	214	213	190
5	2	0	159	163	50
6	2	0	294	295	-14
7	2	0	100	101	39
8	2	0	96	91	182
9	2	0	216	217	199
10	2	0	49	49	83
1	3	0	445	454	113
2	3	0	548	573	65
3	3	0	280	271	-43
4	3	0	274	277	260
5	3	0	467	478	267
6	3	0	125	126	211
7	3	0	254	262	79
8	3	0	188	194	109
9	3	0	50	39	128
10	3	0	83	82	-61
0	4	0	410	407	-21
1	4	0	297	294	-25
2	4	0	377	375	248
3	4	0	366	369	166
4	4	0	147	144	74
5	4	0	105	106	56
6	4	0	140	141	40
7	4	0	79	77	48
8	4	0	163	169	158
9	4	0	118	115	206
10	4	0	51	64	204
1	5	0	372	375	91
2	5	0	303	305	106
3	5	0	32	33	199
4	5	0	259	262	262
5	5	0	142	148	220
6	5	0	26	29	-48
7	5	0	198	199	97
8	5	0	80	77	114
9	5	0	64	60	-20
0	6	0	273	271	-2
1	6	0	196	198	-37
2	6	0	166	168	163
3	6	0	290	291	178
4	6	0	158	164	165
5	6	0	116	116	-16
6	6	0	289	296	7
7	6	0	86	86	32
8	6	0	104	111	223
9	6	0	129	124	168
1	7	0	69	67	180
2	7	0	168	167	111
3	7	0	65	67	-82
5	7	0	200	203	269
6	7	0	97	96	78
7	7	0	153	158	109
8	7	0	124	123	92
0	8	0	164	167	-40
1	8	0	76	73	3
2	8	0	174	176	222
3	8	0	187	186	185
4	8	0	120	116	143
5	8	0	143	152	10
6	8	0	208	207	11
7	8	0	52	52	20
1	9	0	227	229	94
2	9	0	174	175	95
3	9	0	64	69	60
4	9	0	160	160	252
5	9	0	86	90	-67
0	10	0	120	124	21
1	10	0	37	35	54
2	10	0	50	57	149
3	10	0	172	170	196
4	10	0	51	56	248
5	10	0	114	115	-4
1	11	0	107	110	86
2	11	0	105	110	113
3	11	0	76	72	161
-10	0	1	77	78	185
-9	0	1	180	181	185
-8	0	1	88	90	184
-6	0	1	246	239	4
-5	0	1	218	215	2
-4	0	1	295	291	182
-3	0	1	536	542	182
-2	0	1	522	540	181
2	0	1	124	122	-6
3	0	1	26	35	213
4	0	1	198	193	182
5	0	1	174	170	4
6	0	1	101	98	10
8	0	1	203	204	183
9	0	1	157	155	185
-11	1	1	87	92	115
-10	1	1	88	86	101
-9	1	1	75	74	221
-8	1	1	216	213	-82
-7	1	1	153	148	260
-6	1	1	63	62	234
-5	1	1	402	399	115
-4	1	1	596	603	66
-3	1	1	296	292	0
-2	1	1	500	501	-58
1	1	1	268	266	119
2	1	1	292	290	148
3	1	1	286	277	191
4	1	1	390	387	-82
5	1	1	229	233	-59
6	1	1	68	69	114
7	1	1	209	212	108
8	1	1	153	150	95
9	1	1	102	98	-62
10	1	1	106	103	267
-10	2	1	111	111	151
-9	2	1	178	176	188
-8	2	1	105	105	173
-7	2	1	170	172	-22
-6	2	1	270	280	-15
-5	2	1	233	231	23
-4	2	1	261	261	181
-3	2	1	426	426	171
-2	2	1	151	148	85
-1	2	1	81	81	-38
0	2	1	432	438	-42
1	2	1	106	108	-20
2	2	1	140	140	97
3	2	1	334	331	184
4	2	1	170	168	193
5	2	1	241	243	8
6	2	1	286	291	-10
7	2	1	43	42	82
8	2	1	161	157	199
9	2	1	152	158	175
10	2	1	69	67	73
-10	3	1	84	90	85
-9	3	1	65	64	-75
-8	3	1	211	217	261
-7	3	1	265	276	266
-6	3	1	77	76	46
-5	3	1	330	337	82
-4	3	1	441	436	101
-3	3	1	180	174	16
-2	3	1	164	169	-49
-1	3	1	288	287	-67
0	3	1	294	294	180
1	3	1	339	345	133
2	3	1	167	170	46
3	3	1	97	94	197
4	3	1	344	342	-73
5	3	1	351	359	-78
6	3	1	84	85	89
7	3	1	218	223	90
8	3	1	103	104	118
9	3	1	41	24	131
-10	4	1	62	63	219
-9	4	1	156	159	169
-8	4	1	67	65	135
-7	4	1	61	64	39
-6	4	1	143	147	10
-5	4	1	161	158	62
-4	4	1	204	202	188
-3	4	1	457	456	193
-2	4	1	100	100	148
-1	4	1	459	467	4
0	4	1	456	458	17
1	4	1	433	423	-52
2	4	1	312	313	208
3	4	1	315	315	198
4	4	1	143	141	256
5	4	1	134	132	26
6	4	1	208	207	38
7	4	1	74	76	75
8	4	1	157	156	144
9	4	1	149	146	187
-10	5	1	107	106	129
-9	5	1	62	61	163
-8	5	1	104	101	254
-7	5	1	131	136	235
-6	5	1	106	103	-5
-5	5	1	207	211	64
-4	5	1	126	130	77
-3	5	1	202	195	15
-2	5	1	444	444	-85
-1	5	1	294	294	253
0	5	1	86	86	79
1	5	1	317	321	78
2	5	1	303	297	98
3	5	1	177	177	219
4	5	1	170	171	247
5	5	1	114	111	265
6	5	1	50	49	160
7	5	1	153	151	93
8	5	1	72	77	79
9	5	1	69	54	-24
-9	6	1	99	100	191
-8	6	1	98	100	173
-7	6	1	122	124	5
-6	6	1	258	267	7
-5	6	1	54	46	261
-4	6	1	135	135	226
-3	6	1	243	241	181
-2	6	1	172	167	162
-1	6	1	263	261	26
0	6	1	242	243	-4
1	6	1	153	157	10
2	6	1	226	220	186
3	6	1	313	319	192
4	6	1	132	139	241
5	6	1	114	112	16
6	6	1	240	241	23
7	6	1	70	67	-9
8	6	1	101	99	199
9	6	1	76	85	162
-8	7	1	109	117	256
-7	7	1	161	168	-84
-6	7	1	78	92	97
-5	7	1	150	149	95
-4	7	1	133	137	68
-3	7	1	56	54	-79
-2	7	1	272	271	-53
-1	7	1	87	87	-78
0	7	1	57	53	133
1	7	1	226	231	96
2	7	1	297	302	110
3	7	1	117	118	252
4	7	1	281	281	267
5	7	1	150	146	-79
7	7	1	160	159	105
8	7	1	111	109	85
-8	8	1	54	65	175
-7	8	1	86	88	-1
-6	8	1	151	153	15
-5	8	1	66	66	53
-4	8	1	163	163	116
-3	8	1	150	148	203
-2	8	1	77	76	209
-1	8	1	85	90	-2
0	8	1	268	266	-35
1	8	1	64	67	-56
2	8	1	191	190	199
3	8	1	220	220	187
4	8	1	110	113	114
5	8	1	113	109	-5
6	8	1	150	147	5
7	8	1	51	61	38
-7	9	1	71	78	-44
-5	9	1	124	126	93
-4	9	1	91	85	87
-3	9	1	85	94	251
-2	9	1	213	213	-72
-1	9	1	262	267	-84
0	9	1	58	58	119
1	9	1	287	285	94
2	9	1	160	158	103
4	9	1	121	119	-89
5	9	1	81	85	-77
-5	10	1	88	92	-8
-4	10	1	128	122	194
-3	10	1	126	124	184
-1	10	1	77	80	-4
0	10	1	195	196	3
1	10	1	54	57	53
2	10	1	147	146	169
3	10	1	155	152	189
5	10	1	90	96	1
-2	11	1	75	79	256
-1	11	1	111	[illegible]	-86
0	11	1	51	47	5
1	11	1	155	145	84
2	11	1	74	73	99
-9	0	2	194	199	184
-8	0	2	113	112	182
-7	0	2	145	136	5
-6	0	2	91	86	11
-5	0	2	61	60	5
-4	0	2	605	606	181
-3	0	2	242	244	184
2	0	2	306	300	183
3	0	2	360	361	183
5	0	2	218	220	4
6	0	2	230	239	4
7	0	2	54	54	178
8	0	2	84	75	189
9	0	2	208	217	183
-11	1	2	75	66	98
-10	1	2	113	114	107
-9	1	2	59	67	174
-8	1	2	248	249	-65
-7	1	2	178	170	253
-6	1	2	73	71	215
-5	1	2	303	292	107
-4	1	2	306	306	86
-3	1	2	231	220	-44
-2	1	2	155	152	176
1	1	2	436	447	76
2	1	2	287	280	140
3	1	2	275	278	236
4	1	2	382	381	262
5	1	2	163	161	-84
6	1	2	120	116	137
7	1	2	141	139	[illegible]
8	1	2	135	132	57
-11	2	2	64	75	-1
-10	2	2	121	112	150
-9	2	2	195	195	194
-8	2	2	118	119	152
-7	2	2	146	147	29
-6	2	2	297	295	-14
-5	2	2	58	57	103
-4	2	2	275	267	237
-3	2	2	221	219	154
-2	2	2	160	155	51
-1	2	2	204	204	-84
0	2	2	371	374	16
1	2	2	164	163	25
2	2	2	335	336	188
3	2	2	350	350	189
4	2	2	87	89	147
5	2	2	342	348	5
6	2	2	128	130	-4
7	2	2	80	78	-51
8	2	2	149	147	178
9	2	2	99	101	190
-10	3	2	70	74	86
-9	3	2	88	85	263
-8	3	2	197	205	-81
-7	3	2	266	267	-85
-6	3	2	164	165	89
-5	3	2	352	350	99
-4	3	2	139	135	132
-3	3	2	51	45	26
-2	3	2	321	321	-87
-1	3	2	141	144	-50
0	3	2	257	247	49
1	3	2	504	505	105
2	3	2	251	253	64
3	3	2	199	198	228
4	3	2	502	499	-89
5	3	2	227	231	261
6	3	2	82	81	114
7	3	2	188	190	64
8	3	2	133	137	112
-10	4	2	93	85	204
-9	4	2	113	112	183
-8	4	2	73	73	172
-7	4	2	79	83	66
-6	4	2	275	273	42
-5	4	2	89	85	36
-4	4	2	221	215	177
-3	4	2	327	332	196
-2	4	2	178	175	207
-1	4	2	387	381	-20
0	4	2	253	251	12
1	4	2	210	204	-20
2	4	2	144	142	198
3	4	2	242	238	185
4	4	2	125	128	-43
5	4	2	89	84	66
6	4	2	156	155	-26
7	4	2	91	90	82
8	4	2	148	145	167
9	4	2	108	115	178
-10	5	2	70	73	124
-8	5	2	112	113	255
-7	5	2	126	123	251
-6	5	2	63	53	134
-5	5	2	250	249	106
-4	5	2	250	248	58
-3	5	2	172	167	-32
-2	5	2	420	419	-85
-1	5	2	291	288	-72
0	5	2	217	219	63
1	5	2	191	187	80
2	5	2	291	287	124
3	5	2	168	165	268
4	5	2	101	92	-84
5	5	2	168	160	214
6	5	2	45	43	127
7	5	2	190	187	97
-9	6	2	102	102	187
-8	6	2	53	46	187
-7	6	2	184	190	19
-6	6	2	224	223	16
-5	6	2	56	55	-74
-4	6	2	171	174	203
-3	6	2	337	337	167
-2	6	2	155	151	241
-1	6	2	260	257	-9
0	6	2	285	282	-4
1	6	2	146	150	55
2	6	2	242	236	161
3	6	2	247	239	205
4	6	2	103	101	155
5	6	2	128	127	-14
6	6	2	215	217	7
7	6	2	66	68	268
8	6	2	76	77	170
-8	7	2	137	139	-88
-7	7	2	121	127	-75
-6	7	2	74	74	140
-5	7	2	148	146	107
-4	7	2	208	209	87
-3	7	2	37	41	-28
-2	7	2	228	222	-64
-1	7	2	96	93	-47
0	7	2	95	97	-68
1	7	2	233	230	94
2	7	2	145	142	130
3	7	2	53	47	-69
4	7	2	160	160	256
5	7	2	108	109	267
6	7	2	59	60	212
7	7	2	116	111	100
-7	8	2	125	120	3
-6	8	2	162	162	12
-5	8	2	68	72	42
-4	8	2	129	131	149
-3	8	2	235	238	195
-2	8	2	104	104	121
-1	8	2	156	154	-13
0	8	2	210	209	-19
1	8	2	51	43	262
2	8	2	201	204	222
3	8	2	138	134	172
4	8	2	71	61	160
5	8	2	131	127	4
6	8	2	111	112	8
-5	9	2	159	174	84
-4	9	2	114	112	94
-3	9	2	77	81	253
-2	9	2	283	282	-81
-1	9	2	247	251	265
0	9	2	115	112	80
1	9	2	153	148	103
2	9	2	132	125	79
4	9	2	86	86	264
5	9	2	64	58	-67
-6	10	2	94	100	11
-5	10	2	106	100	-15
-4	10	2	132	127	195
-3	10	2	134	139	180
-2	10	2	77	74	180
-1	10	2	121	113	19
0	10	2	122	125	4
1	10	2	43	21	70
2	10	2	62	58	191
3	10	2	108	118	203
-1	11	2	115	111	-88
0	11	2	46	55	116
1	11	2	129	127	81
2	11	2	75	65	123
-10	0	3	67	71	188
-9	0	3	169	162	185
-7	0	3	102	104	7
-6	0	3	224	218	4
-5	0	3	100	95	179
-4	0	3	377	373	182
-3	0	3	601	602	182
1	0	3	52	60	1
2	0	3	37	43	201
3	0	3	111	112	188
4	0	3	148	148	180
5	0	3	149	153	5
6	0	3	67	74	10
7	0	3	66	52	0
8	0	3	126	128	185
9	0	3	166	171	184
-11	1	3	79	69	88
-10	1	3	116	114	132
-9	1	3	126	123	-63
-8	1	3	165	165	266
-7	1	3	66	61	243
-6	1	3	113	116	142
-5	1	3	284	281	90
-4	1	3	213	210	52
-3	1	3	163	165	254
0	1	3	297	294	81
1	1	3	451	451	105
2	1	3	78	76	52
3	1	3	126	124	238
4	1	3	266	261	-67
5	1	3	118	116	249
6	1	3	94	93	180
7	1	3	127	129	91
8	1	3	89	95	114
9	1	3	104	106	-81
-10	2	3	103	90	196
-9	2	3	170	166	197
-8	2	3	61	59	93
-7	2	3	212	215	-17
-6	2	3	67	62	38
-5	2	3	94	89	61
-4	2	3	286	284	166
-3	2	3	189	187	162
-2	2	3	137	137	233
-1	2	3	339	337	-29
0	2	3	429	432	6
1	2	3	84	81	-84
2	2	3	267	267	177
3	2	3	278	275	170
5	2	3	151	153	13
6	2	3	174	168	-18
8	2	3	125	123	199
9	2	3	76	69	192
-11	3	3	132	133	101
-9	3	3	59	57	241
-8	3	3	305	304	-77
-7	3	3	133	132	252
-6	3	3	173	169	54
-5	3	3	215	217	87
-4	3	3	260	258	105
-3	3	3	50	47	0
-2	3	3	292	285	255
-1	3	3	276	277	-74
0	3	3	281	277	139
1	3	3	324	323	85
2	3	3	271	273	57
3	3	3	140	134	-83
4	3	3	240	241	-88
5	3	3	188	189	266
6	3	3	55	57	84
7	3	3	125	130	103
8	3	3	53	63	146
-11	4	3	94	83	-53
-10	4	3	71	80	194
-9	4	3	97	94	214
-8	4	3	42	37	207
-7	4	3	130	125	47
-6	4	3	156	160	0
-5	4	3	201	200	106
-4	4	3	210	210	172
-3	4	3	329	330	172
-2	4	3	102	100	-23
-1	4	3	299	298	8
0	4	3	210	214	-8
1	4	3	253	254	-76
2	4	3	276	277	197
3	4	3	86	88	194
4	4	3	51	46	-23
5	4	3	102	108	6
6	4	3	172	170	25
7	4	3	76	65	120
8	4	3	147	146	175
-10	5	3	91	107	121
-8	5	3	57	64	-90
-7	5	3	172	170	260
-6	5	3	98	100	77
-5	5	3	225	225	74
-4	5	3	126	125	103
-3	5	3	73	63	247
-2	5	3	372	378	-89
-1	5	3	60	60	-36
0	5	3	147	147	20
1	5	3	217	218	96
2	5	3	96	101	64
3	5	3	101	103	-72
4	5	3	171	172	233
5	5	3	98	90	248
6	5	3	96	86	114
7	5	3	163	158	106
-10	6	3	106	116	193
-9	6	3	125	123	192
-8	6	3	59	60	142
-7	6	3	160	158	16
-6	6	3	241	246	4
-5	6	3	83	81	258
-4	6	3	171	171	136
-3	6	3	213	211	190
-2	6	3	79	81	192
-1	6	3	207	208	0
0	6	3	165	164	-4
2	6	3	164	161	213
3	6	3	231	235	174
5	6	3	168	164	18
6	6	3	132	128	12
7	6	3	59	33	264
-8	7	3	126	132	267
-7	7	3	90	96	-74
-6	7	3	48	45	149
-5	7	3	155	157	[illegible]

Table 6. Continued.

-4	7	3	63	63	73
-3	7	3	96	92	247
-2	7	3	114	115	-31
-1	7	3	75	77	-63
0	7	3	119	113	97
1	7	3	150	152	95
2	7	3	121	124	97
3	7	3	165	166	-89
4	7	3	216	216	269
6	7	3	72	75	88
7	7	3	135	141	106
-8	8	3	72	49	193
-7	8	3	111	111	1
-6	8	3	148	152	21
-5	8	3	103	104	44
-4	8	3	113	111	171
-3	8	3	107	105	169
-2	8	3	43	25	206
-1	8	3	98	103	7
0	8	3	132	125	-32
1	8	3	71	70	250
2	8	3	138	136	191
3	8	3	156	159	187
5	8	3	150	148	-20
-7	9	3	74	86	-83
-6	9	3	62	67	124
-5	9	3	151	162	93
-4	9	3	108	108	76
-3	9	3	94	102	-83
-2	9	3	213	216	-78
-1	9	3	99	91	-82
0	9	3	63	70	155
1	9	3	139	137	84
2	9	3	62	61	111
4	9	3	107	103	-76
5	9	3	73	55	-78
-6	10	3	108	113	11
-5	10	3	71	63	-42
-4	10	3	118	111	183
-3	10	3	109	108	197
-2	10	3	60	51	-15
-1	10	3	41	52	13
0	10	3	95	90	19
1	10	3	65	61	95
2	10	3	138	137	188
-1	11	3	82	81	269
0	11	3	69	72	31
1	11	3	117	107	109
2	11	3	54	56	107
-10	0	4	69	56	191
-9	0	4	121	123	185
-7	0	4	190	182	4
-6	0	4	179	178	4
-4	0	4	404	402	182
0	0	4	102	103	8
1	0	4	46	52	-2
2	0	4	97	95	189
3	0	4	65	60	192
5	0	4	221	224	4
6	0	4	129	122	5
7	0	4	65	73	182
8	0	4	134	127	185
-11	1	4	105	93	104
-10	1	4	42	28	101
-9	1	4	85	83	265
-8	1	4	194	193	-78
-7	1	4	138	142	245
-6	1	4	56	61	142
-5	1	4	323	320	96
-4	1	4	224	220	96
-3	1	4	143	147	-90
0	1	4	135	137	56
1	1	4	189	189	106
2	1	4	112	112	148
3	1	4	98	102	-87
4	1	4	179	186	-88
5	1	4	92	89	-67
6	1	4	137	132	121
7	1	4	123	129	78
8	1	4	55	32	151
-10	2	4	116	116	169
-9	2	4	140	135	169
-7	2	4	139	137	-16
-6	2	4	174	175	-18
-5	2	4	48	45	16
-4	2	4	245	246	189
-3	2	4	228	225	158
-2	2	4	104	104	87
-1	2	4	153	158	0
0	2	4	261	267	-6
1	2	4	64	62	208
2	2	4	151	155	211
3	2	4	197	197	174
4	2	4	69	65	-1
5	2	4	176	183	10
6	2	4	83	79	10
7	2	4	52	52	214
8	2	4	123	117	188
-11	3	4	109	100	81
-10	3	4	65	54	105
-9	3	4	133	129	251
-8	3	4	193	190	-88
-7	3	4	103	102	268
-6	3	4	106	104	66
-5	3	4	205	207	100
-4	3	4	139	135	102
-3	3	4	197	199	-31
-2	3	4	209	203	-90
-1	3	4	89	86	257
0	3	4	243	248	107
1	3	4	228	223	92
2	3	4	86	86	92
3	3	4	149	147	231
4	3	4	291	300	-75
5	3	4	49	47	-48
6	3	4	89	83	76
7	3	4	117	106	108
-10	4	4	94	101	181
-9	4	4	72	75	212
-7	4	4	91	91	6
-6	4	4	197	204	18
-5	4	4	82	79	120
-4	4	4	256	255	198
-3	4	4	219	229	175
-2	4	4	102	103	88
-1	4	4	228	233	13
0	4	4	167	168	8
1	4	4	109	115	-72
2	4	4	162	163	164
3	4	4	166	169	237
4	4	4	99	92	-79
5	4	4	119	121	16
6	4	4	104	109	14
7	4	4	67	62	123
-9	5	4	55	46	259
-8	5	4	139	137	224
-7	5	4	94	98	237
-6	5	4	134	132	73
-5	5	4	187	192	96
-4	5	4	112	110	31
-3	5	4	153	151	-49
-2	5	4	294	295	268
0	5	4	96	99	98
1	5	4	168	170	92
2	5	4	81	82	79
3	5	4	140	140	270
4	5	4	90	89	-78
5	5	4	79	82	255
6	5	4	115	119	118
7	5	4	116	109	99
-9	6	4	85	89	173
-7	6	4	174	171	2
-6	6	4	98	99	8
-5	6	4	61	58	189
-4	6	4	98	95	178
-3	6	4	192	191	189
-2	6	4	45	36	-23
-1	6	4	250	246	13
0	6	4	142	137	-3
1	6	4	47	50	70
2	6	4	230	230	191
3	6	4	170	171	195
4	6	4	39	44	-47
5	6	4	123	120	23
6	6	4	114	111	-1
-8	7	4	106	106	264
-7	7	4	60	55	-79
-6	7	4	91	90	119
-5	7	4	82	83	99
-4	7	4	58	60	94
-3	7	4	78	81	-65
-2	7	4	178	176	-54
-1	7	4	99	92	260
0	7	4	105	92	85
1	7	4	233	236	90
2	7	4	108	100	120
3	7	4	143	144	-87
4	7	4	122	122	267
-7	8	4	103	101	-3
-6	8	4	59	72	25
-4	8	4	94	95	161
-3	8	4	93	93	168
-2	8	4	92	88	64
-1	8	4	156	157	-2
0	8	4	156	156	-28
1	8	4	72	74	206
2	8	4	167	167	198
3	8	4	120	123	186
4	8	4	55	36	27
5	8	4	107	98	-23
-6	9	4	81	83	114
-5	9	4	153	137	86
-3	9	4	122	106	269
-2	9	4	186	186	-73
-1	9	4	97	99	265
0	9	4	85	93	68
1	9	4	142	138	86
-1	10	4	84	88	3
0	10	4	123	121	9
-10	0	5	73	70	189
-9	0	5	134	139	184
-7	0	5	200	204	4
-6	0	5	95	88	7
-5	0	5	54	53	183
-4	0	5	319	318	183
0	0	5	289	300	2
1	0	5	101	104	182
2	0	5	95	95	189
3	0	5	176	174	183
5	0	5	205	204	4
6	0	5	63	53	9
-10	1	5	50	61	98
-9	1	5	64	64	-70
-8	1	5	156	153	-81
-7	1	5	83	81	228
-6	1	5	83	75	124
-5	1	5	159	154	84
-4	1	5	76	81	180
0	1	5	190	194	91
1	1	5	232	235	99
2	1	5	57	51	-21
3	1	5	139	143	256
4	1	5	203	192	-71
5	1	5	89	84	187
6	1	5	93	87	98
-10	2	5	68	67	185
-9	2	5	130	125	184
-8	2	5	60	49	45
-7	2	5	74	83	17
-6	2	5	90	102	7
-5	2	5	62	67	154
-4	2	5	153	157	208
-3	2	5	70	69	154
-2	2	5	56	54	269
-1	2	5	236	242	-17
0	2	5	185	189	49
1	2	5	63	65	240
2	2	5	267	270	177
3	2	5	84	85	181
4	2	5	74	85	0
5	2	5	131	126	10
6	2	5	82	84	-31
-10	3	5	65	53	140
-9	3	5	90	90	-85
-8	3	5	188	190	-74
-7	3	5	82	82	239
-6	3	5	108	109	89
-5	3	5	194	186	118
-4	3	5	77	80	39
-3	3	5	56	56	-70
-2	3	5	270	270	269
-1	3	5	43	42	0
0	3	5	147	152	82
1	3	5	225	228	90
2	3	5	134	129	97
3	3	5	182	185	267
4	3	5	149	141	268
5	3	5	58	58	-90
6	3	5	63	58	119
-9	4	5	74	75	254
-8	4	5	43	50	144
-7	4	5	139	146	23
-6	4	5	113	120	30
-5	4	5	93	90	184
-4	4	5	144	144	187
-3	4	5	150	146	168
-2	4	5	88	84	-19
-1	4	5	133	136	14
0	4	5	105	101	-14
1	4	5	71	68	123
2	4	5	135	140	202
3	4	5	62	66	213
4	4	5	73	75	-13
5	4	5	98	95	-1
6	4	5	81	86	0
-9	5	5	61	55	254
-8	5	5	90	94	264
-7	5	5	90	87	262
-6	5	5	175	172	116
-5	5	5	134	134	99
-4	5	5	91	91	86
-3	5	5	154	153	-85
-2	5	5	164	162	-80
-1	5	5	99	97	-23
0	5	5	109	113	54
1	5	5	128	127	107
3	5	5	81	75	-71
4	5	5	124	129	256
5	5	5	59	49	194
-8	6	5	48	40	-12
-7	6	5	149	151	27
-6	6	5	125	124	-9
-4	6	5	159	158	169
-3	6	5	185	180	195
-1	6	5	197	191	-8
0	6	5	130	127	20
2	6	5	126	123	188
3	6	5	113	117	188
4	6	5	51	53	73
5	6	5	97	95	-2
-8	7	5	58	63	-85
-6	7	5	57	58	180
-5	7	5	139	147	99
-3	7	5	50	51	-70
-2	7	5	147	148	-71
-1	7	5	57	49	-49
0	7	5	103	105	81
1	7	5	118	123	95
3	7	5	103	102	-34
-4	8	5	117	122	132
-3	8	5	122	126	154
-1	8	5	144	147	7
0	8	5	87	78	-25
2	8	5	109	109	204
3	8	5	65	67	176
-5	9	5	127	125	94
-4	9	5	93	86	70
-3	9	5	127	125	-29
-2	9	5	152	154	-80
-1	9	5	76	64	241
0	9	5	53	51	100
1	9	5	81	71	87
-7	0	6	132	128	5
-6	0	6	64	59	8
-5	0	6	69	74	184
-4	0	6	216	215	184
0	0	6	90	91	5
2	0	6	71	75	100
-8	1	6	108	105	-74
-7	1	6	42	36	170
-6	1	6	95	92	90
-5	1	6	148	148	106
-4	1	6	40	42	161
-1	1	6	24	40	-55
0	1	6	180	181	97
1	1	6	149	149	96
-7	2	6	98	100	-20
-6	2	6	50	40	13
-5	2	6	65	56	141
-4	2	6	171	177	168
-3	2	6	122	125	165
-2	2	6	63	64	-24
-1	2	6	190	199	2
0	2	6	139	139	-13
1	2	6	123	119	215
2	2	6	127	125	176
-6	3	6	74	76	76
-5	3	6	97	105	96
-4	3	6	73	71	104
-3	3	6	127	135	-22
-2	3	6	144	149	267
0	3	6	148	151	105
1	3	6	151	149	83
-1	4	6	132	133	6
0	4	6	82	85	6
1	4	6	66	66	224
-3	5	6	86	83	262
-2	5	6	113	124	258
-1	5	6	36	32	42
0	5	6	66	68	106
1	5	6	96	94	60
-1	6	6	128	129	14
0	6	6	51	35	-4
1	6	6	45	35	254
0	7	6	99	99	89
1	7	6	113	96	86
-4	8	6	109	96	145
-2	8	6	56	53	19
-1	8	6	69	79	10
0	8	6	63	56	-53
-1	0	7	70	78	9
0	0	7	40	59	5
0	1	7	82	91	107
1	1	7	109	70	79
-3	2	7	99	102	147
-2	2	7	76	80	17
-1	2	7	82	89	12
0	2	7	56	46	22
1	2	7	74	73	214
-1	3	7	49	45	112
0	3	7	87	93	78
1	3	7	117	113	108
-1	4	7	122	109	1
0	4	7	45	22	51
0	5	7	104	101	110

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by conventional Patterson/Fourier methods. The three dimensional Patterson function revealed unambiguously the position of the cobalt atom. The origin was defined using the x and z coordinates for this atom calculated from the Co – Co peak in the Harker section $P(u,\frac{1}{2},w)$. The y coordinate was arbitrarily set to $y = 0$.

Image seeking methods based upon cobalt as a searcher atom revealed an octahedron of oxygen atoms surrounding cobalt.

A series of Fourier syntheses and structure factor calculations revealed the positions of all remaining oxygen and carbon atoms. One of the two possible enantiomorphs was chosen arbitrarily.

The coordinates and anisotropic temperature factors were refined using the Mo$K\alpha$ data and a block-diagonal least squares program. The R-factor at the end of this refinement was 0.034.

All 10 hydrogen atoms were found from difference-Fourier syntheses. Further refinement in which the hydrogen atoms were assumed to have isotropic temperature factors, reduced the R-factor to 0.028.

An absorption correction was introduced. Also an empirical correction for extinction was tried, but it was without significant effect. The final R-value attained was 0.028.

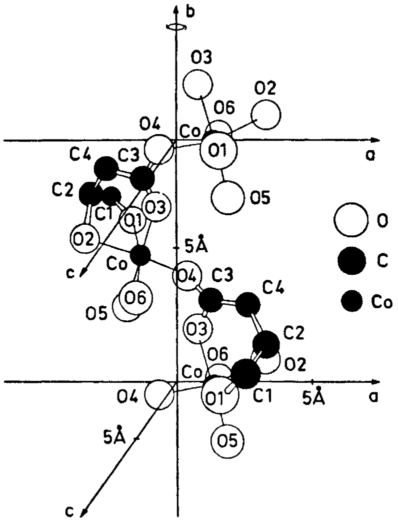

b
03
02
06
04
Co
01
a
C4
C3
C2
C1
03
01
02
5Å
c
Co
06
05
05
04
C3
C4
03
C2
06
02
Co
01
C1
5Å
a
04
5Å
05
c
O
C
Co

Fig. 1. Cobalt(II) (−)-malate trihydrate. Projection of the structure showing the tridentate malate group connecting the cobalt-oxygen octahedra. The malate oxygen (O_7) which does not co-ordinate to cobalt is left out.

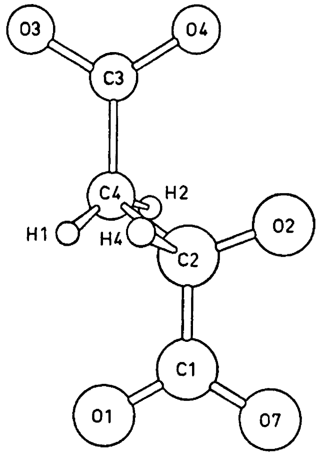

03
04
C3
C4
H2
H1
H4
02
C2
C1
01
07

Fig. 2. The malate group of (−)-malic acid in the absolute configuration as determined from the structure of cobalt(II) (−)-malate trihydrate. The conformation shown differs from the conformation in the complex.

COMPUTATIONAL DETAILS

The reduction of all diffractometer data was performed using an ALGOL program G 404.[4] The other programs used were the following: A Fourier program by Lauesen,[5] structure factor program D 445 by Danielsen,[6] least squares program G 403 by Grønbæk Hazell,[7] and Well's absorption program.[8]

The atomic scattering curves used were for Co, O, and C, calculated as averages of the curves given by Cromer and Waber,[9] and Cromer and Mann.[10] The scattering curve for H was that given by Stewart, Davidson and Simpson.[11] The scattering curves were represented by Bassi[12] polynomials. At the end of the refinement the scattering curves for Co, O, and C were corrected for anomalous dispersion effects (Cromer[13]). The correction terms for Cu$K\alpha$-radiation given in the same paper were used during the investigation of the Cu$K\alpha$ data.

The weighting scheme used for the least squares refinement was: $1/w = (\sigma_c(F^2) + (1+a)F_o^2)^{\frac{1}{2}} - |F_o|$ with $F^2 > 2\sigma_c(F^2)$ and otherwise zero. The parameter a, initially chosen to be 0.020, was subject to refinement and the final value attained was 0.023. An analysis of $\sum w_i(F_o^i - F_c^i)^2$ as a function of $|F_o^i|$ and $(\sin \theta/\lambda)^2$ showed smooth distributions indicating the validity of the weighting scheme.

Bond lengths and angles were computed by means of a program written by J. Danielsen and J. Nyborg.[14]

The absolute configuration was found by comparing the intensities of the 20 independent Friedel pairs observed with those calculated for the arbitrarily selected enantiomorph. Of these 12 pairs showed unequivocally that the chosen

Table 7. Comparison of intensities used in the determination of absolute configuration. The ratio $q = I(hkl)/I(\overline{hkl})$ is given as observed and as calculated.

hkl	q(obs)	$\sigma(q)$	q(calc)	*hkl*	q(obs)	$\sigma(q)$	q(calc)
$250/\bar{2}\bar{5}0$	1.33	0.022	1.27	$420/\bar{4}\bar{2}0$	1.13	0.027	1.08
$\bar{2}50/2\bar{5}0$	1.18	0.023	1.27	$\bar{4}20/4\bar{2}0$	1.18	0.031	1.08
$150/\bar{1}\bar{5}0$	1.00	0.012	0.99	$320/\bar{3}\bar{2}0$	1.15	0.017	1.15
$\bar{1}50/1\bar{5}0$	0.96	0.013	0.99	$\bar{3}20/3\bar{2}0$	1.24	0.021	1.15
$340/\bar{3}\bar{4}0$	0.78	0.010	0.75	$220/\bar{2}\bar{2}0$	0.82	0.008	0.81
$\bar{3}40/3\bar{4}0$	0.77	0.011	0.75	$\bar{2}20/2\bar{2}0$	0.81	0.009	0.81
$240/\bar{2}\bar{4}0$	1.45	0.015	1.49	$120/\bar{1}\bar{2}0$	0.87	0.004	0.83
$\bar{2}40/2\bar{4}0$	1.52	0.017	1.49	$\bar{1}20/1\bar{2}0$	0.89	0.005	0.83
$140/\bar{1}\bar{4}0$	0.81	0.010	0.78	$020/0\bar{2}0$	2.05	0.016	1.91
$\bar{1}40/1\bar{4}0$	0.84	0.012	0.78	$510/\bar{5}\bar{1}0$	0.54	0.021	0.56
$040/0\bar{4}0$	0.72	0.007	0.67	$\bar{5}10/5\bar{1}0$	0.63	0.026	0.56
$430/\bar{4}\bar{3}0$	0.74	0.014	0.73	$410/\bar{4}\bar{1}0$	1.00	0.011	1.03
$\bar{4}30/4\bar{3}0$	0.80	0.017	0.73	$\bar{4}10/4\bar{1}0$	1.10	0.013	1.03
$330/\bar{3}\bar{3}0$	1.05	0.014	1.03	$310/\bar{3}\bar{1}0$	0.99	0.008	0.98
$\bar{3}30/3\bar{3}0$	1.09	0.017	1.03	$\bar{3}10/3\bar{1}0$	1.06	0.010	0.98
$230/\bar{2}\bar{3}0$	0.81	0.005	0.80	$210/\bar{2}\bar{1}0$	0.52	0.004	0.48
$\bar{2}30/2\bar{3}0$	0.81	0.006	0.80	$\bar{2}10/2\bar{1}0$	0.55	0.005	0.48
$130/\bar{1}\bar{3}0$	1.28	0.009	1.27	$110/\bar{1}\bar{1}0$	1.12	0.004	1.19
$\bar{1}30/1\bar{3}0$	1.30	0.010	1.27	$\bar{1}10/1\bar{1}0$	1.10	0.006	1.19

absolute configuration was the correct one, *i.e.* the ratio $I_o(hk0)/I_o(\overline{hk}0)$ differed less that 3 standard deviations from $I_c(hk0)/I_c(\overline{hk}0)$ whereas it differed more than 3 standard deviations from $I_c(\overline{hk}0)/I_c(hk0)$. None of the remaining 8 Friedel pairs showed any contradiction. The results are shown in Table 7.

The calculations were all carried out at Aarhus University's Computing Centre except for the absorption correction which was carried out at NEUCC at Lundtofte.

DISCUSSION

The structure is characterized by the octahedral coordination of oxygen by cobalt as shown in Fig. 1. Four oxygens, O_1, O_2, O_3, and O_4 in an octahedron, belong to malate groups. The remaining O_5 and O_6 belong to water molecules. The octahedra are bridged together by the group $O_3-C_3-O_4$. An infinite spiral of malate groups is thus formed round the *b*-axis, leaving the malate group somewhat strained ($C_3-C_4-C_2$ 117.7°). Two oxygen atoms O_8 belonging to a water molecule and O_7 belonging to the malate group are not coordinated by cobalt. The structure is similar to those of Co(II) and Zn(II) aspartate trihydrate described by Doyne, and Pepinsky and Watanabe.[15]

The cobalt-oxygen distances fall within the range from 2.07 to 2.09 Å except for the $Co-O_2$ distance which is 2.14 Å, standard deviation 0.003 Å, probably due to the strain in the malate group.

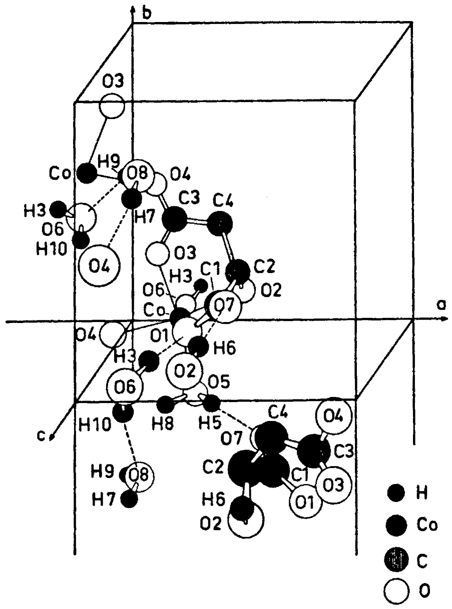
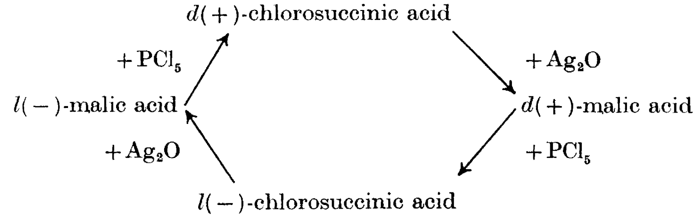


Fig. 3. Hydrogen bonds in cobalt(II) (−)-malate trihydrate. The broken lines indicate hydrogen bonds.

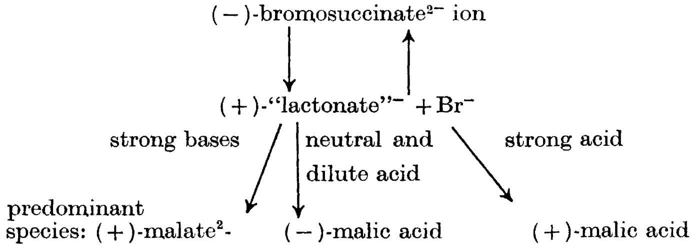
The carbon-carbon and carbon-oxygen distances are in agreement with those for ammonium hydrogen tartrate determined by Bommel and Bijvoet.[16] The structure is hydrogen bonded as shown in Fig. 3.

The classical description of the Walden inversion dating back to 1896 is the following:



Walden[17] repeats this description in his monograph from 1919 and it has been faithfully quoted in numerous textbooks ever since.

In 1913 Holmberg[18] showed by careful kinetic experiments that the hydrolysis of bromo- or chlorosuccinic acid in neutral solutions proceeds *via* an intermediate not containing halogen. Holmberg proposed that the intermediate were a β-lactone. He found that solutions containing as much as 75 % of the intermediate could be prepared. If the intermediate prepared from (−)-bromosuccinic acid is hydrolysed in strongly alkaline solution 60 %−70 % of (+)-malate ions and 30 %−40 % of (−)-malate ions are produced. This is also the case if enough Ag_2O is added to make the solution sufficiently alkaline. In dilute acid or in neutral solution (−)-malic acid is the dominating species. The silver salts of halogen succinic acids and of malic acid are sparingly soluble. The reactions of halogen succinic acids with Ag_2O have mostly resulted in heterogeneous reactions in a neutral environment and it is apparently the acidity of the solution and not the presence of silver which determines the chirality of the malic acid produced in the reaction. Holmberg's results have been confirmed by Rørdam[19] who has extended the investigations to hydrolysis in strongly acidic solutions. His and Holmberg's results can be summarized as follows:



Ingold *et al.*[20] assumed that the lactone was formed with inversion of configuration whereas the alkaline hydrolysis should retain configuration.

Since we now know with certainty that (−)-chlorosuccinic acid and (−)-malic acid have the same chirality, the reaction path from (−)-chlorosuccinic acid to (+)-malic acid must involve an odd number of inversions whereas the production of (−)-malic acid from (−)-chlorosuccinic acid must involve an even number of inversions. None of the reactions quoted yield pure compounds. Fumaric acid is often formed in smaller or greater amounts and the highest yields obtained of one particular enantiomorph are about 70 %. No reaction mechanism has so far been described which explains the percentages of enantiomers obtained in the various reactions. Malic acid and the halogen succinic acids themselves racemize very slowly under the conditions of the experiments quoted from the literature. Thus three or four molecules of malic acid of one chirality are formed more or less simultaneously with two of the opposite chirality in the hydrolysis of bromo- or chlorosuccinic acid. Since the chemistry of the Walden inversion is rather complex, we cannot point to one single reaction which will retain or invert configuration. As correlation of configurations is of high importance in organic chemistry we shall summarize the results of well documented X-ray investigations employing anomalous scattering on carboxylic acids containing four carbon atoms:

Compounds of similar chirality:

(–)-chlorosuccinic acid [2]	(*S*-configuration)
(–)-malic acid	(*S*-configuration)
(–)-tartaric acid [21]	(2*S*,3*S*-configuration)

Chemical correlations of configurations based on reactions where Walden inversion does not take place are in agreement with the crystallographic results.

Acknowledgements. The authors are indebted to *Carlsberg Fondet* for the linear diffractometer and to Mrs. R. Grønbæk Hazell for advice on computational problems.

REFERENCES

1. Walden, P. *Ber.* **29** (1896) 133.
2. Kryger, L., Danielsen, J. and Rasmussen, S. E. *Acta Chem. Scand.* **26** (1972) 2339.
3. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
4. Grønbæk Hazell, R. *Program G 404,* Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C. Denmark.
5. Lauesen, S. *Fourier Machine Order Program,* "Regnecentralen", Copenhagen.
6. Danielsen, J. *Program D 445,* Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.
7. Grønbæk Hazell, R. *Program G 403,* Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.
8. Wells, M. J. *Acta Cryst.* **13** (1970) 722.
9. Cromer, D. T. and Waber, J. T. *Acta Cryst* **18** (1965) 104.
10. Cromer, D. T. and Mann, J. B. *Acta Cryst.* **A 24** (1968) 321.
11. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
12. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
13. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
14. Danielsen, J. and Nyborg, J. *General Distance and Angle program,* Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C. Denmark.
15. Doyne, T., Pepinsky, R. and Watanabe, T. *Acta Cryst.* **10** (1957) 438.
16. van Bommel, A. J. and Bijvoet, J. M. *Acta Cryst.* **11** (1958) 61.
17. Walden, P. *Optische Umkehrscheinungen,* Vieweg & Sohn, Braunschweig 1919.
18. Holmberg, B. *J. prakt. Chem.* N. F. **87** (1913) 471.
19. Rørdam, H. N. K. *J. Chem. Soc.* **1932** 2931.
20. Cowdrey, W. A., Hughes, E. D., Ingold, C. K., Mastermann, S. and Scott, A. D. *J. Chem. Soc.* **1937** 1252.
21. Peerdemann, A. F., van Bommel, A. J., and Bijvoet, J. M. *Proc. Kon. Ned. Akad. Wetensch.* **B 54** (1951) 16.

Received October 25, 1971.