Table 9 *(cont.)*

		(r.m.s.) (Å)	$\cos\alpha_{1j}$	$\cos\alpha_{2j}$	$\cos\alpha_{3j}$
C(3)	2	0·163	0·424	0·740	−0·520
	3	0·238	0·793	−0·027	0·607
	1	0·116	−0·562	−0·309	0·766
C(4)	2	0·205	−0·478	0·878	0·004
	3	0·257	0·674	0·364	0·642
	1	0·189	−0·667	0·000	−0·744
C(5)	2	0·260	0·052	−0·997	−0·046
	3	0·327	0·742	0·070	−0·666
	1	0·204	−0·544	−0·148	0·825
C(6)	2	0·217	0·585	0·637	0·500
	3	0·263	−0·600	0·755	−0·259
	1	0·223	0·356	0·097	−0·929
C(7)	2	0·257	−0·375	−0·895	−0·238
	3	0·332	0·855	−0·433	0·282
	1	0·268	0·402	0·091	−0·910
C(8)	2	0·369	−0·842	−0·351	−0·407
	3	0·455	0·357	−0·931	0·064
	1	0·219	0·126	0·673	0·727
C(9)	2	0·340	−0·104	0·738	−0·665
	3	0·395	0·986	−0·008	−0·164

The root-mean-square displacement (r.m.s.)$_j$ is directed along the jth axes of the ellipsoid where α_{1j}, α_{2j} and α_{3j} are the angles between the jth axis and the a, b and c^* axes, respectively.

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The Crystal and Molecular Structure of Bis(hydrogen *o*-phthalato)diaquocopper(II)

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Bis(hydrogen *o*-phthalato)diaquocopper(II), $Cu(C_8H_5O_4)_2(H_2O)_2$, is monoclinic, $P2_1/c$: $a=8{\cdot}31$ (2), $b=14{\cdot}62$ (2), $c=7{\cdot}20$ (2) Å, $\beta=112{\cdot}2$ (0·2)°, $Z=2$. The crystal structure has been determined at room temperature from three-dimensional X-ray photographic data and refined by differential methods with anisotropic thermal parameters to a final R value of 7·9%. Two oxygen atoms from two carboxyl groups of two different phthalate ions and two H_2O molecules coordinate with copper in a centrosymmetrical planar arrangement [Cu–O(1) = 1·930 (8), Cu–O(5) = 1·967 (8) Å]. Two further oxygen atoms, from the same Cu-coordinated carboxyl groups, are involved in two weaker interactions with the metal atom [Cu–O(2) = 2·677 (5) Å], so the coordination polyhedron can be considered also as an elongated and distorted octahedron. The two carboxyl groups are slightly rotated with respect to the benzene ring, in opposite directions from each other and their relative position is determined by a strong intramolecular hydrogen bond, O(2)H···O(3) = 2·42 Å. Packing is mainly determined by two hydrogen bonds formed by the water molecule with the oxygen atoms from the carboxyl groups of two adjacent molecules: O(5)H···O(3^{i}) = 2·81, O(5)H···O(4^{ii}) = 2·67 Å.

Introduction

Bis(hydrogen *o*-phthalato)diaquocopper(II), $[Cu(C_8H_5O_4)_2(H_2O)_2]$, crystallizes from acid aqueous solutions in beautiful monoclinic crystals (Cingi & Magnano, 1959), suitable for single-crystal X-ray analysis. The study of their structure was considered to be interesting because it

should help to find the way *o*-phthalate anion coordinates to metal, particularly in connexion with the influence of the steric-hindrance effects on coordination.

Experimental

The compound gives blue pleochroic (blue when the electric vector is parallel to the elongation of the crystals, azure when perpendicular) monoclinic prisms elongated along [001]. Cell constants, determined from rotation and Weissenberg photographs, are as follows, (standard deviations are given in parentheses):

$[Cu(C_8H_5O_4)_2(H_2O)_2]$, $M=429{\cdot}8$;
$a=8{\cdot}31(2)$, $b=14{\cdot}62(2)$, $c=7{\cdot}20(2)$ Å,
$\beta=112{\cdot}2°(0{\cdot}2°)$; $V=809{\cdot}2$ Å^3; $Z=2$, $D_m=1{\cdot}81$, $D_x=1{\cdot}76$ g.cm^{-3}; $\mu=25{\cdot}0$ cm^{-1} (Cu $K\alpha$); $F(000)=438$.
Space group: $P2_1/c$ (from systematic absences).

Three-dimensional intensity data were determined photometrically on integrated equi-inclination Weissenberg photographs (multiple-film technique; Cu $K\alpha$) taken up to the seventh and sixth layers along [100] and [001] respectively. Of the 1721 possible independent reflexions within the Cu $K\alpha$ sphere, 1288 were collected, the remaining 433 reflexions being too weak to be estimated, or unobservable owing to the geometrical features of the camera. After correction for Lorentz, polarization and spot shape effects (Phillips, 1956) the absorption correction was taken into account considering the samples as spherical ($\bar{r}=0{\cdot}02$ cm) and cylindrical ($\bar{r}=0{\cdot}006$ cm) for the reflexions taken around [100] and [001] respectively. The data of both series were correlated and put on a common scale by the least-squares procedure of Rollett & Sparks (1960). The absolute scale was determined first by Wilson's (1942) method, then by comparison of the observed and calculated structure factors.

Structure determination and refinement

Since two molecules of $[Cu(C_8H_5O_4)_2(H_2O)_2]$ are contained in a unit cell, they must be on a symmetry centre. Two sets of interactions between the Cu atom and light-atoms, the result of a Patterson mirror parallel to (010), are present in vector space; chemical criteria were successfully applied to distinguish between these two sets. Two three-dimensional Fourier cycles yielded the locations of all the non-hydrogen atoms ($R=15{\cdot}2\%$). The refinement was then carried out by means of six cycles of Booth's differential synthesis, two calculated with isotropic and four with anisotropic thermal parameters ($R=8{\cdot}4\%$).

While the location of the four benzene and the two water hydrogen atoms was possible from a final F_o-F_c synthesis, any attempt to locate the hydrogen atom of the uncoordinated carboxyl group was unsuccessful, the peak resulting from that atom being too spread out in the region between the two oxygen atoms. The fractional atomic coordinates for the hydrogen atoms located in this way are given in Table 1 with their electron density values, determined by differential synthesis.

Table 1. *Observed fractional coordinates and corresponding values for hydrogen atoms in the benzene ring and water molecule*

	x/a	*y/b*	*z/c*	ϱ_0
H(1)	0·5249	0·0547	0·1671	1·0 e.Å^{-3}
H(2)	0·8105	0·1193	0·2297	1·2
H(3)	0·8481	0·2868	0·2334	0·9
H(4)	0·6044	0·3894	0·1754	0·5
H(5)	0·0010	−0·0679	0·3447	1·4
H(6)	0·1278	0·0104	0·3923	0·6

By adding the contributions of the hydrogen atoms quoted in Table 1 (with the isotropic temperature factor of the carbon or oxygen atoms to which they are attached) to the structure factors, the residual error indices, R and R', improved to 7·9% and 9·3% respectively (R for observed reflexions only, R' assuming $F_o=\frac{1}{2}F_{min}$ when $F_c \geq F_{min}$ for unobserved reflexions; multiplicities not considered).

In Table 2 the final parameters with their e.s.d.'s (Cruickshank, 1949, 1950, 1956) and the ratios between the e.s.d.'s and the shifts of the coordinates are quoted. The B_{ij}'s were determined following the method of Nardelli & Fava (1960) by the use of the second derivatives

Table 2. *Final atomic fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10$ Å^2) *with e.s.d.'s and ratios (e.s.d.)/(coordinate shift)*

	x/a	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	|r(x)|	|r(y)|	|r(z)|
Cu	0 (1)	0 (1)	0 (2)	26 (1)	21 (0)	34 (2)	−4 (1)	11 (2)	−1 (1)	∞	∞	∞
O(1)	2303 (7)	475 (2)	551 (10)	19 (4)	17 (0)	37 (6)	−5 (3)	10 (6)	−2 (3)	12	5	19
O(2)	1042 (8)	1717 (2)	1115 (11)	22 (5)	23 (0)	47 (8)	0 (3)	17 (8)	0 (4)	7	10	53
O(3)	1395 (8)	3363 (2)	1209 (9)	26 (5)	21 (0)	39 (7)	4 (3)	13 (7)	−1 (4)	26	2	23
O(4)	3147 (8)	4341 (2)	561 (11)	27 (4)	18 (0)	39 (6)	0 (3)	5 (7)	4 (4)	∞	2	18
O(5)	598 (9)	−298 (3)	2848 (9)	33 (4)	33 (0)	33 (7)	−16 (3)	10 (7)	0 (3)	8	10	21
C(1)	2350 (9)	1320 (3)	994 (11)	20 (5)	19 (0)	22 (7)	0 (4)	8 (7)	3 (4)	9	5	36
C(2)	3990 (10)	1836 (3)	1354 (11)	16 (4)	15 (0)	19 (6)	0 (3)	5 (7)	1 (4)	4	10	9
C(3)	4207 (10)	2814 (3)	1375 (10)	15 (4)	16 (0)	21 (6)	−2 (3)	5 (6)	−1 (3)	2	4	102
C(4)	2855 (9)	3558 (3)	1007 (10)	22 (5)	19 (0)	21 (6)	0 (4)	4 (7)	−1 (4)	∞	7	8
C(5)	5420 (10)	1259 (3)	1677 (11)	21 (5)	21 (0)	30 (8)	2 (4)	10 (8)	1 (5)	19	3	28
C(6)	7054 (11)	1617 (4)	2057 (13)	17 (5)	27 (1)	38 (9)	2 (4)	9 (9)	−1 (5)	21	2	6
C(7)	7268 (11)	2580 (4)	2075 (13)	21 (5)	29 (1)	31 (8)	−3 (4)	7 (8)	−1 (5)	37	2	15
C(8)	5852 (10)	3163 (3)	1719 (11)	21 (5)	22 (0)	29 (8)	−4 (4)	6 (8)	1 (4)	13	2	28

of the electron density from differential synthesis. In Table 3 the observed atomic peak shapes for non-hydrogen atoms are compared with the calculated ones. Observed and calculated (including the H atoms of Table 1) structure factors are reported in Table 4. The atomic scattering factors used are those of Thomas & Umeda (1957) for Cu^{2+}, of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O and C and of McWeeny (1951) for H. The standard deviations quoted in the next section are calculated

Table 3. *Atomic peak heights* (e. Å^{-3}) *and curvatures* (e. Å^{-5})

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Cu	obs.	66·3	628	699	574	−15	209	−34
	calc.	66·0	627	693	581	−16	211	−27
O(1)	obs.	13·2	130	147	95	−2	37	−14
	calc.	13·0	130	145	97	−2	37	−13
O(2)	obs.	13·0	122	133	95	−11	43	6
	calc.	12·7	119	133	97	−11	42	6
O(3)	obs.	13·6	123	124	110	−5	45	7
	calc.	13·4	123	123	111	−4	45	6
O(4)	obs.	12·9	102	128	87	4	28	−2
	calc.	12·8	103	127	89	3	30	−1
O(5)	obs.	13·1	100	97	118	6	37	−13
	calc.	12·8	102	97	117	5	37	−9
C(1)	obs.	9·4	93	106	86	−6	30	4
	calc.	9·7	93	106	86	−6	30	4
C(2)	obs.	10·0	93	94	95	−5	35	5
	calc.	10·0	92	93	95	−5	35	5
C(3)	obs.	10·1	94	92	99	−3	36	−4
	calc.	10·3	93	91	100	−3	37	−4
C(4)	obs.	10·4	93	98	97	−2	33	−4
	calc.	10·4	93	97	98	−2	34	−4
C(5)	obs.	9·5	88	92	94	6	25	−5
	calc.	9·6	88	92	85	6	25	−5
C(6)	obs.	8·7	81	74	68	−4	24	2
	calc.	8·7	79	76	69	−5	24	2
C(7)	obs.	9·0	79	79	72	0	25	−5
	calc.	8·9	78	79	72	−1	25	−5
C(8)	obs.	9·6	84	98	81	1	25	−9
	calc.	9·6	84	97	82	1	25	−8
	e.s.d.	0·2	2	2	2	1	1	1

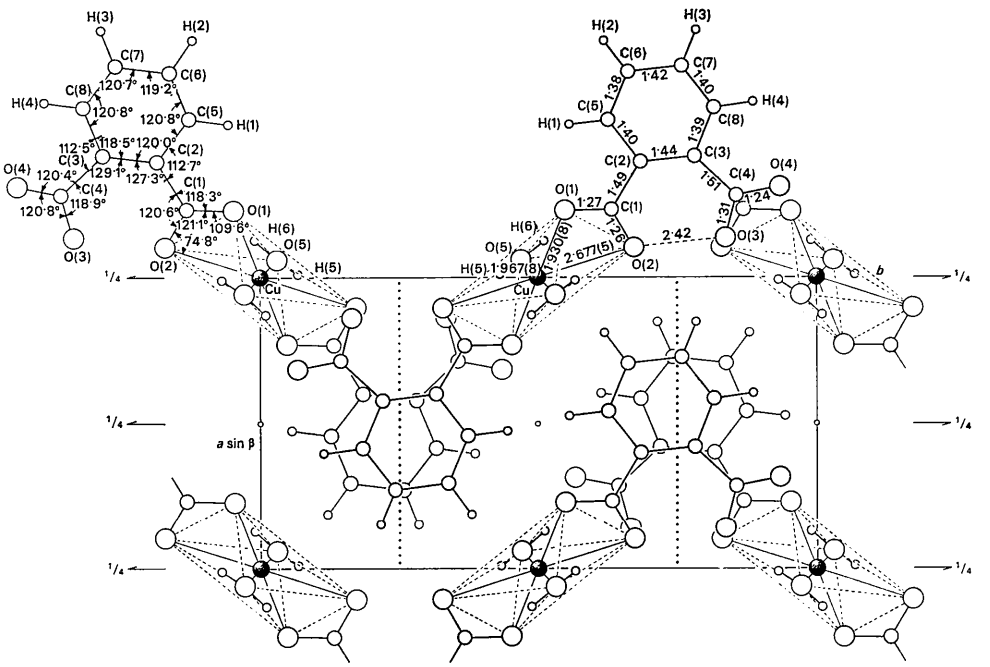

Fig. 1. $[Cu(C_8H_5O_4)_2(H_2O)_2]$: projection of the structure along [001].

from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles, the effects of errors in cell parameters being accounted for by the method of Darlow & Cochran (1961).

All the calculations were performed on the Olivetti Elea 6001/S computer of the *Centro di Calcolo Elettronico della Università di Parma*, using the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965).

Discussion

A projection of the structure along [001] is shown in Fig. 1. Bond distances and angles in the coordination polyhedron and in the organic ion are quoted in Table 5.

Four oxygen atoms from two phthalate ions and two water molecules coordinate to the metal atom in a

Table 4. *Observed and calculated structure factors*

h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$
1	0	0	280	285	7	10	0	126	98	0	4	1	134	109	8	9	1	18-	15	1	17	-1	157	172	2	5	2	61	-55	8	10	-2	87	110
2	0	0	22-	8	8	10	0	69	81	1	4	1	215	191	0	10	1	103	93	2	17	1	142	148	2	5	-2	119	-96	9	10	-2	11-	0
3	0	0	472	465	1	11	0	180	146	1	4	-1	253	-240	1	10	1	42-	16	2	17	-1	84	82	3	5	2	53	-60	0	11	2	168	144
4	0	0	388	344	2	11	0	164	158	2	4	1	188	-159	1	10	-1	188	-176	3	17	1	65	80	3	5	-2	337	310	1	11	2	219	219
5	0	0	111	96	3	11	0	168	155	2	4	-1	329	-304	2	10	1	38-	-5	3	17	-1	69	79	4	5	2	215	-197	1	11	-2	42-	25
6	0	0	111	-111	4	11	0	80	76	3	4	1	461	416	2	10	-1	84	-88	0	18	1	26-	-30	4	5	-2	84	74	2	11	2	211	-215
7	0	0	376	366	5	11	0	57-	-44	3	4	-1	38	-18	3	10	1	333	324	1	18	1	22-	0	5	5	2	107	-102	2	11	-2	91	70
8	0	0	115	101	6	11	0	50-	-20	4	4	1	150	129	3	10	-1	115	100	1	18	-1	22-	-16	5	5	-2	46	43	3	11	2	80	-78
9	0	0	99	107	7	11	0	77	73	4	4	-1	257	209	4	10	1	138	-121	2	18	-1	18-	47	6	5	2	77	-77	3	11	-2	115	-125
1	1	0	454	-481	8	11	0	26-	-35	5	4	1	223	-218	4	10	-1	42-	-57	0	0	2	154	171	6	5	-2	57	-63	4	11	2	46-	33
2	1	0	333	-328	0	12	0	249	232	5	4	-1	122	85	5	10	1	42-	16	1	0	2	299	-233	7	5	2	77	88	4	11	-2	160	140
3	1	0	257	-205	1	12	0	322	310	6	4	1	38-	-20	5	10	-1	119	101	1	0	-2	886	1280	7	5	-2	95	-93	5	11	2	130	-135
4	1	0	77	58	2	12	0	180	171	6	4	-1	30-	-34	6	10	1	61	-59	2	0	2	180	-121	8	5	2	46	68	5	11	-2	130	128
5	1	0	160	141	3	12	0	234	231	7	4	1	61	-61	6	10	-1	80	84	2	0	-2	280	258	8	5	-2	38-	-27	6	11	2	26-	-10
6	1	0	50-	-10	4	12	0	65-	7	7	4	-1	99	97	7	10	1	30	-24	3	0	2	311	286	9	5	-2	30-	-8	6	11	-2	134	-140
7	1	0	168	149	5	12	0	57-	7	8	4	1	34-	-20	7	10	-1	26-	-41	3	0	-2	319	303	0	6	2	195	183	7	11	-2	46	-55
8	1	0	73-	22	6	12	0	188	195	8	4	-1	38-	28	8	10	-1	26-	54	4	0	2	315	286	1	6	2	207	198	8	11	-2	22-	16
9	1	0	57-	8	7	12	0	184	203	9	4	1	69	-70	0	11	1	238	228	4	0	-2	333	352	1	6	-2	591	609	0	12	2	172	149
0	2	0	95	115	1	13	0	176	180	9	4	-1	30-	-39	1	11	1	215	196	5	0	2	303	290	2	6	2	46	37	1	12	2	223	232
1	2	0	672	954	2	13	0	142	-144	0	5	1	399	401	1	11	-1	238	232	5	0	-2	157	190	2	6	-2	641	664	1	12	-2	203	191
2	2	0	376	432	3	13	0	184	-192	1	5	1	299	301	2	11	1	437	452	6	0	2	268	239	3	6	2	87	74	2	12	2	199	190
3	2	0	530	530	4	13	0	57-	68	1	5	-1	564	624	2	11	-1	164	150	6	0	-2	268	270	3	6	-2	299	300	2	12	-2	457	484
4	2	0	626	606	5	13	0	154	150	2	5	1	307	300	3	11	1	111	96	7	0	2	184	188	4	6	2	226	214	3	12	2	42-	-32
5	2	0	292	251	6	13	0	57	56	2	5	-1	260	269	3	11	-1	472	512	7	0	-2	154	-133	4	6	-2	307	285	3	12	-2	341	363
6	2	0	341	348	7	13	0	38	31	3	5	1	264	243	4	11	1	157	145	8	0	2	99	129	5	6	2	226	225	4	12	2	38-	35
7	2	0	77	-74	0	14	0	138	101	3	5	-1	722	760	4	11	-1	50-	-38	8	0	-2	211	226	5	6	-2	150	141	4	12	-2	87	95
8	2	0	107	88	1	14	0	99	88	4	5	1	215	180	5	11	1	61	66	0	1	2	1272	-1481	6	6	2	160	163	5	12	2	160	176
9	2	0	146	155	2	14	0	99	85	4	5	-1	319	296	5	11	-1	95	90	1	1	2	337	-290	6	6	-2	61	64	5	12	-2	38-	11
1	3	0	541	-603	3	14	0	195	207	5	5	1	65	55	6	11	1	150	154	1	1	-2	722	-816	7	6	2	176	199	6	12	2	138	171
2	3	0	95	62	4	14	0	195	202	5	5	-1	253	238	6	11	-1	115	103	2	1	2	207	178	7	6	-2	26-	18	6	12	-2	69	74
3	3	0	675	698	5	14	0	95	93	6	5	1	184	185	7	11	1	138	161	2	1	-2	30	-12	8	6	2	87	123	7	12	-2	91	111
4	3	0	211	-168	6	14	0	168	185	6	5	-1	276	258	7	11	-1	176	177	3	1	2	191	155	8	6	-2	195	216	8	12	2	18-	18
5	3	0	42-	13	1	15	0	65	8	7	5	1	115	116	0	12	1	57	-47	3	1	-2	50	47	9	6	-2	142	162	0	13	2	46-	16
6	3	0	50	33	2	15	0	80	77	7	5	-1	154	140	1	12	1	73	-58	4	1	2	34-	26	0	7	2	472	-443	1	13	2	69	-67
7	3	0	50	46	3	15	0	53-	-37	8	5	1	95	106	1	12	-1	172	-183	4	1	-2	357	-306	1	7	2	272	-260	1	13	-2	154	145
8	3	0	73-	10	4	15	0	50-	50	0	6	1	402	382	2	12	1	203	187	5	1	2	73	-69	1	7	-2	30-	-2	2	13	2	91	-86
9	3	0	53-	-21	5	15	0	34-	-10	1	6	1	180	-164	2	12	-1	42-	69	5	1	-2	207	-203	2	7	2	65	-64	2	13	-2	77	73
0	4	0	168	127	0	16	0	207	195	1	6	-1	99	-85	3	12	1	99	-98	6	1	2	257	263	2	7	-2	80	-64	3	13	2	42-	-20
1	4	0	541	609	1	16	0	53-	26	2	6	1	115	99	3	12	-1	77	-77	6	1	-2	99	-121	3	7	2	50	-34	3	13	-2	42-	-78
2	4	0	518	587	2	16	0	115	104	2	6	-1	299	-271	4	12	1	50-	-5	7	1	2	138	-139	3	7	-2	119	-104	4	13	2	103	102
3	4	0	545	524	3	16	0	130	135	3	6	1	65	32	4	12	-1	77	-92	7	1	-2	184	211	4	7	2	142	129	4	13	-2	168	-186
4	4	0	376	345	4	16	0	119	133	3	6	-1	30-	-2	5	12	1	73	65	8	1	2	26-	-29	4	7	-2	337	-327	5	13	2	26-	22
5	4	0	380	374	1	17	0	46-	24	4	6	1	95	84	5	12	-1	38-	-5	8	1	-2	38-	-13	5	7	2	38-	-34	5	13	-2	65	-47
6	4	0	154	133	2	17	0	57	55	4	6	-1	34-	29	6	12	1	73	73	9	1	-2	34-	32	5	7	-2	80	-83	6	13	2	11-	15
7	4	0	119	104	3	17	0	87	89	5	6	1	61	-72	6	12	-1	84	85	0	2	2	648	750	6	7	2	38-	38	6	13	-2	30-	19
8	4	0	111	104	0	18	0	142	151	5	6	-1	80	-70	7	12	1	38	-48	1	2	2	103	122	6	7	-2	138	-145	7	13	-2	57	48
9	4	0	50-	51	1	18	0	107	116	6	6	1	57	-59	7	12	-1	69	59	1	2	-2	61	91	7	7	2	22-	-18	0	14	2	257	256
1	5	0	138	132	3	18	0	22-	42	6	6	-1	77	75	8	12	-1	11-	-44	2	2	2	154	147	7	7	-2	53	48	1	14	2	84	71
2	5	0	561	603	0	1	1	483	519	7	6	1	46	54	0	13	1	50-	-4	2	2	-2	353	-281	8	7	2	15-	-7	1	14	-2	215	209
3	5	0	238	212	1	1	1	445	459	7	6	-1	42	30	1	13	1	341	362	3	2	2	706	681	8	7	-2	61	57	2	14	2	199	206
4	5	0	211	175	1	1	-1	496	561	8	6	1	61	-60	1	13	-1	87	91	3	2	-2	150	-90	9	7	-2	26-	51	2	14	-2	38-	33
5	5	0	57	-38	2	1	1	115	116	9	6	-1	30-	-30	2	13	1	230	229	4	2	2	288	274	0	8	2	126	108	3	14	2	203	226
6	5	0	46	-21	2	1	-1	648	690	0	7	1	499	499	2	13	-1	307	310	4	2	-2	541	531	1	8	2	426	427	3	14	-2	142	155
7	5	0	134	-133	3	1	1	91	-64	1	7	1	288	288	3	13	1	199	212	5	2	2	180	173	1	8	-2	134	130	4	12	2	84	91
8	5	0	69	69	3	1	-1	337	337	1	7	-1	77	76	3	13	-1	107	114	5	2	-2	349	342	2	8	2	361	358	4	14	-2	138	155
9	5	0	61	66	4	1	1	472	406	2	7	1	337	334	4	13	1	107	118	6	2	2	126	129	2	8	-2	392	372	5	14	2	18-	0
0	6	0	839	953	4	1	-1	533	616	2	7	-1	380	374	4	13	-1	107	109	6	2	-2	223	228	3	8	2	311	300	5	14	-2	138	146
1	6	0	587	646	5	1	1	280	257	3	7	1	322	296	5	13	1	122	129	7	2	2	138	144	5	8	-2	91	81	6	14	-2	57	66
2	6	0	487	515	5	1	-1	518	618	3	7	-1	514	498	5	13	-1	119	126	7	2	-2	322	351	4	8	2	138	122	7	14	-2	115	153
3	6	0	195	175	6	1	1	142	-126	4	7	1	230	219	6	13	1	111	124	8	2	2	99	134	4	8	-2	138	127	0	15	2	61	58
4	6	0	50-	15	6	1	-1	292	289	4	7	-1	299	264	6	13	-1	115	122	8	2	-2	134	138	5	8	2	160	171	1	15	2	38-	26
5	6	0	203	179	7	1	1	142	136	5	7	1	154	148	7	13	-1	95	102	0	3	2	288	-277	5	8	-2	322	316	1	15	-2	80	84
6	6	0	107	93	7	1	-1	65	-57	5	7	-1	234	211	0	14	1	107	110	1	3	2	333	-314	6	8	2	53	57	2	15	2	34-	13
7	6	0	234	230	8	1	1	199	212	6	7	1	57	43	1	14	1	91	91	1	3	-2	223	-195	6	8	-2	215	217	2	15	-2	34-	-15
8	6	0	142	156	9	1	1	119	140	6	7	-1	284	283	1	14	-1	91	98	2	3	2	219	195	7	8	2	91	108	3	15	2	30-	-25
9	6	0	53	59	0	2	1	119	-103	7	7	1	142	147	2	14	1	42-	53	2	3	-2	238	-203	7	8	-2	157	160	3	15	-2	38-	18
1	7	0	364	-346	1	2	1	215	176	7	7	-1	142	140	2	14	-1	42-	13	3	3	2	34-	-15	8	8	-2	146	165	4	15	2	38	-50
2	7	0	146	-134	1	2	-1	130	-119	8	7	1	69	78	3	14	1	91	-99	3	3	-2	22-	5	9	8	-2	22-	54	4	15	-2	34-	-33
3	7	0	57	38	2	2	1	146	-126	8	7	-1	34-	35	3	14	-1	42-	21	4	3	2	195	-173	0	9	2	138	-106	5	15	-2	26-	16
4	7	0	130	107	2	2	-1	280	-274	0	8	1	84	-60	4	14	1	38-	-20	4	3	-2	223	173	1	9	2	199	-186	6	15	-2	61	68
5	7	0	95	84	3	2	1	42	41	1	8	1	146	129	4	14	-1	99	-107	5	3	2	42	45	1	9	-2	38-	-42	0	16	2	138	158
6	7	0	126	114	3	2	-1	172	-149	1	8	-1	299	-268	5	14	1	73	73	5	3	-2	176	-173	2	9	2	99	87	1	16	2	142	147
7	7	0	119	114	4	2	1	34-	12	2	8	1	138	138	5	14	-1	34-	-15	6	3	2	77	-75	2	9	-2	249	-221	1	16	-2	150	166
8	7	0	91	56	4	2	-1	355	315	2	8	-1	107	-96	6	14	1	15-	31	6	3	-2	26-	37	3	9	2	87	75	2	16	2	77	79
9	7	0	38-	-61	5	2	1	115	-95	3	8	1	87	-70	6	14	-1	80	79	7	3	2	38	28	3	9	-2	37	4	2	16	-2	84	89
0	8	0	46-	30	5	2	-1	188	-180	3	8	-1	34-	-20	7	14	-1	11-	-45	7	3	-2	142	-145	4	9	2	207	-211	3	16	2	164	195
1	8	0	341	322	6	2	1	150	-146	4	8	1	42-	23	0	15	1	122	129	8	3	2	53	58	4	9	-2	199	187	3	16	-2	84	93
2	8	0	322	312	6	2	-1	272	-280	4	8	-1	99	101	1	15	1	172	169	8	3	-2	84	77	5	9	2	38-	-17	4	16	-2	180	195
3	8	0	234	219	7	2	1	230	219	5	8	1	103	-97	1	15	-1	142	152	9	3	-2	77	76	5	9	-2	211	-221	5	16	-2	22-	45
4	8	0	510	507	7	2	-1	122	128	5	8	-1	107	-97	2	15	1	168	170	0	4	2	249	245	6	9	2	30-	12	0	17	2	30-	2
5	8	0	211	173	8	2	1	53	45	6	8	1	38-	-11	2	15	-1	184	184	1	4	2	453	467	6	9	-2	38-	-1	1	17	2	57	61
6	8	0	203	199	9	2	1	46	-46	6	8	-1	134	-143	3	15	1	61	87	1	4	-2	119	-86	7	9	2	22	31	1	17	-2	65	-61
7	8	0	142	130	9	2	-1	34-	49	7	8	1	26-	24	3	15	-1	38-	0	2	4	2	587	581	7	9	-2	30-	8	2	17	2	18-	44
8	8	0	111	113	0	3	1	406	428	7	8	-1	122	124	4	15	1	150	165	2	4	-2	84	77	8	9	-2	30-	15	2	17	-2	38	40
9	8	0	22-	58	1	3	1	203	206	8	8	1	61	62	4	15	-1	73	82	3	4	2	61	79	9	9	-2	18-	-16	3	17	-2	34	34
1	9	0	65	22	1	3	-1	557	618	0	9	1	264	257	5	15	1	176	198	3	4	-2	406	396	0	10	2	184	169	4	17	-2	18-	60
2	9	0	50-	-31	2	3	1	69	80	1	9	1	215	204	5	15	-1	115	123	4	4	2	396	352	1	10	2	414	404	0	1	3	361	407
3	9	0	249	231	2	3	-1	422	454	1	9	-1	329	319	6	15	-1	87	95	4	4	-2	69	79	1	10	-2	77	97	1	1	3	522	497
4	9	0	164	142	3	3	1	357	328	2	9	1	215	198	0	16	1	38-	30	5	4	2	211	187	2	10	2	329	324	1	1	-3	499	634
5	9	0	57-	23	3	3	-1	160	182	2	9	-1	292	298	1	16	1	84	94	5	4	-2	399	372	2	10	-2	215	201	2	1	3	272	247
6	9	0	57-	-18	4	3	1	223	205	3	9	1	468	480	1	16	-1	73	73	6	4	2	180	182	3	10	2	130	119	2	1	-3	388	460
7	9	0	80	75	4	3	-1	568	550	3	9	-1	84	65	2	16	1	30-	-22	6	4	-2	299	303	3	10	-2	349	344	3	1	3	303	326
8	9	0	50-	22	5	3	1	253	238	4	9	1	42	37	2	16	-1	34-	-9	7	4	2	50	55	4	10	2	150	153	3	1	-3	107	121
0	10	0	160	-128	5	3	-1	465	458	4	9	-1	384	362	3	16	1	30-	26	7	4	-2	249	276	4	10	-2	164	187	4	1	3	380	344
1	10	0	164	148	6	3	1	307	297	5	9	1	203	173	3	16	-1	34-	-45	8	4	2	77	108	5	10	2	65	65	4	1	-3	46	57
2	10	0	553	585	6	3	-1	168	150	5	9	-1	42-	9	4	16	1	26-	37	8	4	-2	87	101	5	10	-2	103	106	5	1	3	180	165
3	10	0	234	215	7	3	1	87	84	6	9	1	292	306	4	16	-1	30-	24	9	4	-2	111	127	6	10	2	80	90	5	1	-3	468	482
4	10	0	65-	44	7	3	-1	392	437	6	9	-1	245	241	5	16	-1	61	60	0	5	2	333	322	6	10	-2	180	187	6	1	3	38-	26
5	10	0	349	348	8	3	1	77	86	7	9	1	80	87	0	17	1	154	170	1	5	2	138	-117	7	10	2	80	106	6	1	-3	245	248
6	10	0	160	154	9	3	1	61	41	7	9	-1	249	256	1	17	1	77	76	1	5	-2	268	-260	7	10	-2	157	169	7	1	3	154	165

Table 4 (*cont.*)

h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$	h	k	l	$\lvert 10F_o \rvert$	$10F_c$
7	1	-3	30	0	7	7	-3	134	132	5	14	-3	30-	24	4	4	-4	402	391	8	10	-4	119	132	5	3	5	119	130	3	10	-5	38-	11
8	1	3	95	131	8	7	-3	99	108	6	14	-3	57	48	5	4	4	73	69	0	11	4	107	92	5	3	-5	372	362	4	10	5	30	-34
8	1	-3	38-	69	9	7	-3	30-	12	7	14	-3	11-	37	5	4	-4	142	129	1	11	4	65	-54	6	3	-5	199	192	4	10	-5	160	-153
0	2	3	26-	0	0	8	3	103	-90	0	15	3	38	41	6	4	4	26-	15	1	11	-4	80	-59	7	3	-5	50	-45	5	10	-5	30-	15
1	2	3	160	-142	1	8	3	122	-115	1	15	3	130	143	6	4	-4	260	253	2	11	4	34-	10	8	3	-5	219	205	6	10	-5	26-	-9
1	2	-3	130	117	1	8	-3	38-	-22	1	15	-3	115	125	7	4	-4	146	129	2	11	-4	130	-122	9	3	-5	122	138	7	10	-5	18-	26
2	2	3	150	-131	2	8	3	103	-97	2	15	3	26-	44	8	4	-4	230	220	3	11	4	38	34	0	4	5	65	63	8	10	-5	15-	-27
2	2	-3	65	60	2	8	-3	111	99	2	15	-3	176	175	9	4	-4	115	120	3	11	-4	42-	5	1	4	5	42	-45	0	11	5	95	81
3	2	3	223	194	3	8	3	188	173	3	15	3	84	95	0	5	4	69	-69	4	11	4	30-	-36	1	4	-5	34	22	1	11	5	253	261
3	2	-3	22-	-13	3	8	-3	203	200	3	15	-3	146	161	1	5	4	38-	-32	4	11	-4	46-	33	2	4	5	30-	5	1	11	-5	95	95
4	2	3	42-	25	4	8	3	46-	-29	4	15	-3	34-	35	1	5	-4	399	-388	5	11	4	15-	30	2	4	-5	95	-94	2	11	5	22-	-17
4	2	-3	150	140	4	8	-3	38-	-20	5	15	-3	119	129	2	5	4	38-	-17	5	11	-4	77	70	3	4	5	38-	15	2	11	-5	142	142
5	2	3	146	-136	5	8	3	34-	-14	0	16	3	73	75	2	5	-4	219	-208	6	11	-4	111	109	3	4	-5	107	-108	3	11	5	103	128
5	2	-3	150	138	5	8	-3	184	170	1	16	3	26-	5	3	5	4	80	59	7	11	-4	57	56	4	4	5	84	-92	3	11	-5	34	33
6	2	3	211	201	6	8	3	126	135	1	16	-3	34-	24	3	5	-4	103	88	8	11	-4	38	44	4	4	-5	77	-64	4	11	-5	288	288
6	2	-3	84	-78	6	8	-3	53	-46	2	16	3	22-	-10	4	5	4	46-	-24	0	12	4	134	127	5	4	5	50	-44	5	11	-5	50	27
7	2	3	50	52	7	8	3	50	61	2	16	-3	69	67	4	5	-4	34-	11	1	12	4	50	42	5	4	-5	61	54	6	11	-5	91	94
7	2	-3	299	-318	7	8	-3	150	-152	3	16	-3	57	-60	5	5	4	34	28	1	12	-4	42-	18	6	4	-5	77	-78	7	11	-5	84	94
8	2	3	15-	-39	8	8	-3	34-	-14	4	16	-3	26-	-3	5	5	-4	188	161	2	12	4	115	116	7	4	-5	84	-80	0	12	5	22	32
9	2	-3	34-	18	9	8	-3	26-	32	5	16	-3	18-	37	6	5	4	26-	1	2	12	-4	87	76	8	4	-5	160	159	1	12	5	26-	41
0	3	3	468	485	0	9	3	288	257	0	17	3	42	55	6	5	-4	157	153	3	12	4	119	126	9	4	-5	69	59	1	12	-5	30	33
1	3	3	410	404	1	9	3	188	185	1	17	3	18-	70	7	5	-4	87	101	3	12	-4	207	214	0	5	5	111	106	2	12	5	22-	8
1	3	-3	396	409	1	9	-3	150	150	1	17	-3	122	137	8	5	-4	50	-41	4	12	4	95	113	1	5	5	154	151	2	12	-5	57	-54
2	3	3	322	300	2	9	3	180	164	2	17	-3	87	93	9	5	-4	53	51	4	12	-4	333	332	1	5	-5	199	207	3	12	5	15-	-33
2	3	-3	361	359	2	9		241	232	3	17	-3	99	113	0	6	4	50	-30	5	12	-4	103	101	2	5	5	57	45	3	12	-5	34-	12
3	3	3	399	366	3	9	3	288	291	0	0	4	150	-119	1	6	4	176	172	6	12	-4	46	34	2	5	-5	157	160	4	12	-5	34-	41
3	3	-3	223	212	3	9	-3	329	342	1	0	4	160	-129	1	6	-4	203	181	7	12	-4	103	116	3	5	5	138	139	5	12	-5	77	-83
4	3	3	392	361	4	9	3	77	74	1	0	-4	778	1000	2	6	4	234	217	0	13	4	130	130	3	5	-5	107	112	6	12	-5	22-	-7
4	3	-3	219	213	4	9	-3	211	204	2	0	4	249	239	2	6	-4	376	366	1	13	4	38-	20	4	5	5	73	77	7	12	-5	15-	-3
5	3	3	176	151	5	9	3	154	158	2	0	-4	180	170	3	6	4	126	122	1	13	-4	38-	30	4	5	-5	299	295	0	13	5	188	189
5	3	-3	99	107	5	9	-3	46	34	3	0	4	372	380	3	6	-4	453	451	2	13	4	30-	-41	5	5	5	80	91	1	13	5	91	103
6	3	3	138	139	6	9	3	87	100	3	0	-4	341	366	4	6	4	203	214	2	13	-4	199	199	5	5	-5	184	179	1	13	-5	87	94
6	3	-3	99	89	6	9	-3	103	95	4	0	4	172	173	4	6	-4	380	366	3	13	4	107	115	6	5	-5	199	196	2	13	5	77	91
7	3	3	22	23	7	9	-3	238	259	4	0	-4	644	681	5	6	4	103	101	3	13	-4	38-	9	7	5	-5	191	186	2	13	-5	46	53
7	3	-3	95	87	8	9	-3	84	93	5	0	4	77	-70	5	6	-4	329	319	4	13	-4	38-	-29	8	5	-5	157	149	3	13	-5	191	200
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3	4	-3	199	-177	4	10	3	46	36	0	1	4	134	119	1	7	-4	73	89	2	14	-4	142	130	3	6	-5	157	-145	2	14	-5	22-	17
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7	4	-3	164	168	9	10	-3	15-	56	4	1	-4	30	18	5	7	-4	95	-96	2	15	-4	22-	22	9	6	-5	69	70	4	15	-5	42	48
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7	5	3	119	130	1	12	3	107	99	4	2	4	46-	41	5	8	-4	276	271	3	1	-5	172	199	0	8	5	38-	2	2	1	6	50	48
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1	6	-3	223	206	3	12	-3	238	243	6	2	-4	215	204	9	8	-4	119	127	6	1	5	73	102	3	8	5	30-	-2	4	1	-6	150	155
2	6	3	34-	-29	4	12	3	34-	-12	7	2	4	30	71	0	9	4	46-	27	6	1	-5	341	337	3	8	-5	73	-68	5	1	-6	30-	-2
2	6	-3	80	-69	4	12	-3	126	-132	7	2	-4	241	247	1	9	4	154	126	7	1	-5	272	267	4	8	5	42	-43	6	1	-6	30-	-4
3	6	3	142	120	5	12	3	84	90	8	2	-4	73	55	1	9	-4	77	60	8	1	-5	53	53	4	8	-5	38-	20	7	1	-6	38	-44
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5	6	3	57	48	8	12	-3	18-	20	2	3	4	329	321	3	9	-4	168	-157	2	2	5	30-	46	8	8	-5	18-	19	1	2	-6	345	399
5	6	-3	34-	-1	0	13	3	168	166	2	3	-4	215	-206	4	9	4	80	80	2	2	-5	65	-66	9	8	-5	15-	-14	2	2	6	184	175
6	6	3	34-	-6	1	13	3	211	216	3	3	4	134	-119	4	9	-4	91	95	3	2	5	38-	18	0	9	5	130	125	2	2	-6	57	68
6	6	-3	122	-134	1	13	-3	42-	-4	3	3	-4	26-	26	5	9	4	26-	-23	3	2	-5	111	-113	1	9	5	84	76	3	2	6	91	99
7	6	3	42	47	2	13	3	122	126	4	3	4	46-	1	5	9	-4	195	187	4	2	5	34-	-28	1	9	-5	164	161	3	2	-6	95	102
7	6	-3	57	54	2	13	-3	238	235	4	3	-4	207	194	6	9	-4	61	-61	4	2	-5	30-	-10	2	9	5	315	322	4	2	6	111	116
8	6	-3	42	43	3	13	3	34-	27	5	3	4	38-	-8	7	9	-4	38	34	5	2	5	22-	-8	2	9	-5	126	130	4	2	-6	95	111
9	6	-3	30-	-52	3	13	-3	164	163	5	3	-4	30-	-7	8	9	-4	87	91	5	2	-5	180	168	3	9	5	26-	-12	5	2	-6	91	101
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2	7	3	280	270	6	13	-3	130	140	7	3	-4	69	54	1	10	-4	61	50	8	2	-5	87	-74	5	9	-5	219	216	0	3	6	84	-81
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3	7	-3	329	321	1	14	3	42	-31	0	4	4	480	504	3	10	4	38-	0	1	3	5	95	100	8	9	-5	111	124	2	3	6	77	-71
4	7	3	115	98	1	14	-3	42-	-17	1	4	4	361	363	3	10	-4	260	258	1	3	-5	215	223	9	9	-5	7-	58	2	3	-6	42	-4
4	7	-3	238	220	2	14	3	34-	-31	1	4	-4	319	329	4	10	4	154	165	2	3	5	195	191	0	10	5	30	-26	3	3	6	53	-30
5	7	3	73	80	2	14	-3	115	110	2	4	4	53	59	4	10	-4	119	106	2	3	-5	195	215	1	10	5	34-	27	3	3	-6	22	-15
5	7	-3	172	163	3	14	3	30-	-55	2	4	-4	288	288	5	10	4	80	88	3	3	5	73	79	1	10	-5	65	-64	4	3	6	26-	23
6	7	3	172	189	3	14	-3	57	48	3	4	4	180	164	5	10	-4	38-	24	3	3	-5	176	190	2	10	5	38	40	4	3	-6	87	-84
6	7	-3	249	263	4	14	3	26-	28	3	4	-4	195	188	6	10	4	234	232	4	3	5	57	70	2	10	-5	53	-50	5	3	6	107	102
7	7	3	57	65	4	14	-3	38-	-19	4	4	4	146	143	7	10	-4	154	154	4	3	-5	154	154	3	10	5	61	-67	6	3	-6	53	-53

Table 4 (*cont.*)

h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$
7	3	-6	22-	-19	7	6	-6	122	131	1	10	6	34	39	4	1	-7	73	82	2	5	7	103	95	3	9	-7	91	97	2	3	-8	30-	-44
8	3	-6	80	-74	8	6	-6	57	57	1	10	-6	115	116	5	1	-7	57	63	2	5	-7	77	78	4	9	-7	188	194	3	3	-8	38-	-7
0	4	6	160	167	0	7	6	38-	13	2	10	6	18-	11	6	1	-7	119	132	3	5	-7	138	139	5	9	-7	30-	29	4	3	-8	46-	10
1	4	6	99	101	1	7	6	34-	7	2	10	-6	115	110	7	1	-7	61	71	4	5	-7	46-	58	6	9	-7	103	112	5	3	-8	30-	-16
1	4	-6	219	226	1	7	-6	46	37	3	10	-6	91	98	0	2	7	53-	-4	5	5	-7	154	161	7	9	-7	53	66	6	3	-8	46	41
2	4	6	30-	12	2	7	6	30-	8	4	10	-6	180	184	1	2	7	46-	-5	6	5	-7	77	77	0	10	7	30-	-43	7	3	-8	15	-20
2	4	-6	95	99	2	7	-6	34-	-7	5	10	-6	103	103	1	2	-7	46-	-21	7	5	-7	50	57	2	10	-7	26-	-9	0	4	8	30-	47
3	4	6	146	154	3	7	6	26-	-6	6	10	-6	38	-30	2	2	7	57	54	0	6	7	46-	29	3	10	-7	61	63	1	4	-8	95	115
3	4	-6	103	120	3	7	-6	53	48	7	10	-6	99	107	2	2	-7	42-	70	1	6	7	38-	-20	5	10	-7	61	61	2	4	-8	119	119
4	4	6	73	88	4	7	-6	111	118	0	11	6	30-	22	3	2	7	22-	12	1	6	-7	57	65	6	10	-7	22-	-15	3	4	-8	73	73
4	4	-6	134	142	5	7	-6	34-	3	1	11	6	80	-90	3	2	-7	50-	-13	2	6	7	57	52	2	11	-7	65	71	4	4	-8	57	68
5	4	-6	87	89	6	7	-6	30-	-12	1	11	-6	53	54	4	2	-7	57-	-21	2	6	-7	38-	-17	3	11	-7	84	86	3	4	-8	157	189
6	4	-6	61	57	7	7	-6	99	-99	2	11	6	15-	-37	5	2	-7	42-	-6	3	6	-7	46-	-18	3	12	-7	18-	-35	6	4	-8	53	62
7	4	-6	107	99	8	7	-6	61	-52	2	11	-6	57	56	6	2	-7	80	78	4	6	-7	46-	60	1	0	-8	65	82	7	4	-8	53	64
8	4	-6	99	100	0	8	6	87	91	3	11	-6	53	-57	7	2	-7	57	62	5	6	-7	103	107	2	0	-8	103	107	0	5	8	30-	-27
0	5	6	191	-211	1	8	6	157	162	4	11	-6	84	-91	0	3	7	107	132	6	6	-7	30-	-10	3	0	-8	80	80	1	5	-8	57	75
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1	5	-6	26	23	2	8	6	111	108	6	11	-6	26	27	1	3	-7	146	153	0	7	7	84	90	5	0	-8	91	109	3	5	-8	38-	0
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6	5	-6	30-	-4	8	8	-6	84	84	6	12	-6	95	106	7	3	-7	84	91	7	7	-7	99	111	5	1	-8	46	60	4	6	-8	38-	52
7	5	-6	22-	-5	0	9	6	50	-47	0	13	6	18-	-4	0	4	7	53-	-18	0	8	7	38-	-27	6	1	-8	46	48	5	6	-8	30-	35
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1	6	6	164	176	2	9	6	42	-43	3	13	-6	91	95	2	4	7	26-	-25	2	8	-7	38-	32	1	2	-8	65	86	2	7	-8	26-	-38
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2	6	-6	138	128	3	9	-6	46	-42	0	1	7	119	131	4	4	-7	57-	3	5	8	-7	34-	-34	4	2	-8	130	144	5	7	-8	84	95
3	6	6	111	125	4	9	-6	42	-37	1	1	7	95	94	5	4	-7	111	113	6	8	-7	80	85	5	2	-8	73	70	6	7	-8	18-	-14
3	6	-6	103	97	5	9	-6	77	72	1	1	-7	111	119	6	4	-7	34-	-28	7	8	-7	46	52	6	2	-8	122	134	2	8	-8	22-	44
4	6	6	65	75	6	9	-6	80	-80	2	1	7	119	110	7	4	-7	77	-88	0	9	7	30-	63	7	2	-8	73	86	3	8	-8	84	111
4	6	-6	69	75	7	9	-6	18-	-10	2	1	-7	191	193	0	5	7	119	88	1	9	-7	91	96	0	3	8	30-	22	5	8	-8	18-	38
5	6	-6	234	232	8	9	-6	18-	-10	3	1	7	77	105	1	5	7	91	85	2	9	-7	30-	41	1	3	-8	38-	41	3	9	-8	18-	3
6	6	-6	176	170	0	10	6	191	189	3	1	-7	146	156	1	5	-7	164	171															

A minus sign with F_o means 'less than'.

square-planar arrangement. The difference between the Cu–O(5) and Cu-O(1) distances is just statistically significant ($\Delta/\sigma = 3{\cdot}27$); these two distances can be correlated with the x_g and y_g principal axes of the *g*-ellipsoid respectively, as deduced from the electron spin resonance spectrum (Dall'Olio, Dascola, Giori & Varacca 1968). These two bond distances are within the range of values generally found in oxygen coordinated Cu^{II} complexes, *e.g.* 1·967(4), 1·981(4), 1·991(4) Å in Cu^{II} glutamate dihydrate (Gramaccioli & Marsh, 1966); 1·962(7), 1·975(7), 1·975(6), 1·990(7) Å in Cu^{II} succinate dihydrate (O'Connor & Maslen, 1966); 1·938(15), 1·941(15), 1·983(15), 2·000(15) Å in di-μ-hydroxobis[dimethylaminecopper(II)] sulphate monohydrate (Iitaka, Shimizu & Kwan,1966) and 1·930(7), 1·987(7) Å in glycylglycylglycinocopper(II) chloride sesquihydrate (Freeman, Robinson & Schoone, 1964).

The coordination polyhedron is completed by two longer bonds involving two oxygen atoms, O(2) and O(2′) belonging to the same Cu-coordinated carboxyl groups which are part of a very elongated and severely distorted octahedron. The angle formed by these two long bonds with the coordination plane is 54·3°. This kind of distortion, which is commonly observed for Cu^{II} complexes and is accounted for by Jahn–Teller effect, is also conditioned by the steric requirements concerning the orientation of the organic ions as can be seen from the clinographic projection of Fig. 2.

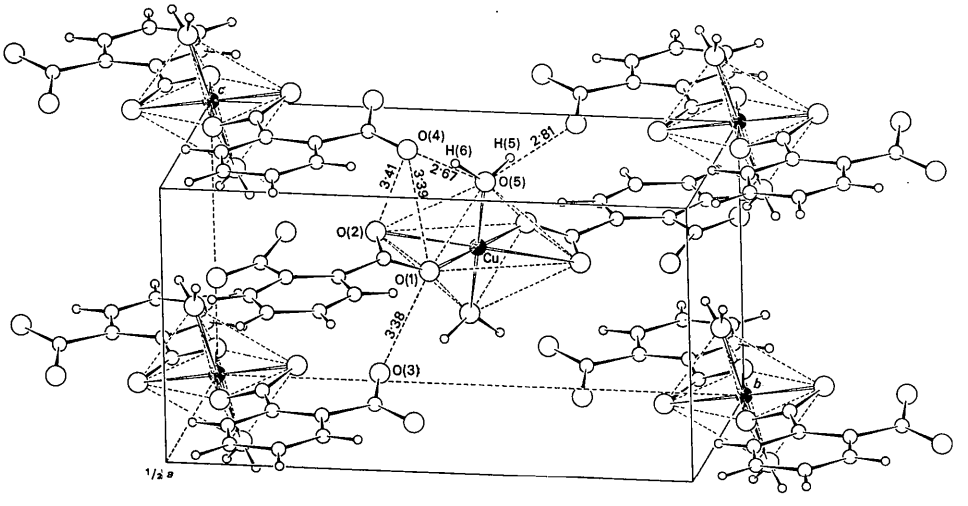

Fig. 2. $[Cu(C_8H_5O_4)_2(H_2O)_2]$: clinographic projection of the structure.

The benzene ring of the phthalate ion is planar, its least-squares equation:

$$0{\cdot}1921X - 0{\cdot}0141Y - 0{\cdot}9813Z = -0{\cdot}3540\,.$$

The carboxyl groups are both planar and slightly rotated around their C–C bonds in opposite directions (the distances of the oxygen atoms from the benzene ring are: O(1), +0·32; O(2), −0·31; O(3), −0·36; O(4), +0·35 Å), the dihedral angle between them being 28·2°. The two C–O distances in the deprotonated carboxyl group are not significantly different and correspond to the average value of the two C–O distances in the other group. The difference between these last two distances is significant; the longer one belongs to the hydroxyl group as usually observed in carboxyl acids (Nardelli, Fava & Giraldi, 1962). A strong intramolecular hydrogen bond, O(2)H···O(3) = 2·422(6) Å, determines the relative orientations of the carboxyl groups which are, for this reason, unable to act as bridges between adjacent metal atoms, as observed in other Cu^{II}-carboxylate complexes, *e.g.* Cu^{II} acetate dihydrate (van Niekerk & Schoening, 1953), Cu^{II} formate tetrahydrate (Kiriyama, Ibamoto & Matsuo, 1954) and Cu^{II} benzoate trihydrate (Koizumi, Osaki & Watanabé, 1963). The same kind of behaviour is observed in Cu^{II} salicylate tetrahydrate (Hanic & Michalov, 1960) in which the OH group is hydrogen-bonded to the carboxyl oxygen atom involved in the long bond with the metal atom.

The bond angle and distances in the water molecule are in quite good agreement with those (HOH = 104·5°, O–H = 0·96 Å) generally found. The orientation of the molecule is determined by the two normal hydrogen bonds it makes with $O(3^{I})$ and $O(4^{II})$: O(5)H(5)···$O(3^{I})$ = 2·81, O(5)H(6)···$O(4^{II})$ = 2·67 Å; H(5)O(5)-$O(3^{I})$ = 13·6°, H(6)O(5)$O(4^{II})$ = 14·8°. The plane of the water molecule is rotated with respect to the O(1)CuO(5) coordination plane, the dihedral angle between these two planes being 46·1°. The angles formed by O–H and Cu–O bonds are: H(5)O(5)Cu = 130·1° and H(6)O(5)Cu = 122·8°.

The organic ions are packed in layers roughly parallel to (001) as shown in Fig. 2. The packing contacts less than 3·5 Å are as follows:

O(1)···$O(3^{iii})$ = 3·38 Å	i,	$\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$
O(1)···$O(4^{II})$ = 3·41	ii,	$x, \frac{1}{2}-y, z+\frac{1}{2}$
O(2)···$O(4^{II})$ = 3·39	iii,	$x, \frac{1}{2}-y, z-\frac{1}{2}$

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Table 5. *Bond distances and angles*

(*a*) In the coordination polyhedron

Cu–O(1)	1·930 (8) Å	O(1)–Cu–O(5)	91·4 (0·3)°
Cu–O(5)	1·967 (8)	O(1)–Cu–O(2)	54·4 (0·2)
Cu–O(2)	2·677 (5)	O(2)–Cu–O(5)	88·2 (0·2)

(*b*) In the phthalate ion

C(1)–O(1)	1·273 (5) Å	C(5)–C(6)	1·382 (12) Å
C(1)–O(2)	1·264 (10)	C(6)–C(7)	1·418 (8)
C(1)–C(2)	1·492 (11)	C(7)–C(8)	1·396 (11)
C(4)–O(3)	1·306 (11)	C(8)–C(3)	1·390 (12)
C(4)–O(4)	1·237 (7)	C(5)–H(1)	1·05 (2)
C(4)–C(3)	1·513 (9)	C(6)–H(2)	1·03 (2)
C(2)–C(3)	1·440 (7)	C(7)–H(3)	1·04 (3)
C(2)–C(5)	1·403 (11)	C(8)–H(4)	1·08 (2)
O(1)–C(1)–O(2)	121·1 (0·7)°	C(5)–C(6)–C(7)	119·2 (0·7)°
O(1)–C(1)–C(2)	118·3 (0·7)	C(6)–C(7)–C(8)	120·7 (0·8)
O(2)–C(1)–C(2)	120·6 (0·4)	C(7)–C(8)–C(3)	120·8 (0·5)
C(1)–C(2)–C(5)	112·7 (0·5)	C(8)–C(3)–C(2)	118·5 (0·6)
C(1)–C(2)–C(3)	127·3 (0·7)	C(2)–C(5)–H(1)	119·4 (1·5)
O(3)–C(4)–O(4)	120·8 (0·6)	C(6)–C(5)–H(1)	119·8 (2·0)
O(3)–C(4)–C(3)	118·9 (0·5)	C(5)–C(6)–H(2)	120·8 (1·6)
O(4)–C(4)–C(3)	120·4 (0·7)	C(7)–C(6)–H(2)	120·1 (2·0)
C(4)–C(3)–C(2)	129·1 (0·7)	C(6)–C(7)–H(3)	120·8 (1·8)
C(4)–C(3)–C(8)	112·5 (0·4)	C(8)–C(7)–H(3)	118·5 (1·5)
C(3)–C(2)–C(5)	120·0 (0·7)	C(7)–C(8)–H(4)	119·6 (1·6)
C(2)–C(5)–C(6)	120·8 (0·5)	C(3)–C(8)–H(4)	119·6 (1·8)

(*c*) In the water molecule

O(5)–H(5)	0·94 (2) Å	H(5)–O(5)–H(6)	103·9 (1·6)°
O(5)–H(6)	0·97 (2)		

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Structure of *p*-Bromocarbobenzoxy-glycyl-prolyl-leucyl-glycine

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The crystal structure of the synthetic oligopeptide, *p*-bromocarbobenzoxy-Gly-L-Pro-L-Leu-Gly(OH), has been determined. The crystal is orthorhombic, space group $P2_12_12_1$, with four molecules per unit cell of dimensions: $a=14{\cdot}25$, $b=6{\cdot}21$ and $c=29{\cdot}67$ Å. The R value is 0·05 and the average of the estimated standard deviations of the bond lengths is 0·025 Å. The peptide chain is folded back at Pro and Leu so as to make the intramolecular hydrogen bond between NH of Gly(2) and O of Gly(1). The conformation of the peptide backbone is very similar to those in some cyclohexapeptides. The Pro residue in this peptide, unlike those in the structure models of collagen, has the C_α–H bond *cis* to the C′=O bond. The particular conformation may be related to the fact that this peptide is inactive against collagenase while carbobenzoxy-Gly-Pro-Leu-Gly-Pro(OH) is active. The strong hydrogen bond between Gly(2) and the oxycarbonyl group links the peptides to form an endless and slightly deformed helical chain.

Introduction

The X-ray studies on a series of oligopeptides, such as carbobenzoxy(*Z*)-Gly, *Z*-Gly-Pro, *Z*-Gly-Pro-Leu, *Z*-Gly-Pro-Leu-Gly and *Z*-Gly-Pro-Leu-Gly-Pro has been carried out as a long range research project in this laboratory, concerning biologically important substances. They were synthesized in order to examine the relationship between the structure of collagen and the substrate specificity of the enzymatic reaction of collagenase (Nagai & Noda, 1959; Nagai, Sakakibara, Noda, Akabari, 1960; Sakakibara & Nagai, 1960; Kakudo, Sasada, Katsube, Sakakibara & Akabori, 1963). It has been recognized that the above mentioned pentapeptide has a high degree of specificity to the reaction while the tetrapeptide has not, and that the sequence of the amino acid residues, such as -Pro-Leu-Gly-Pro-, has an essential importance for the specificity (Nagai & Noda, 1959; Nagai *et al.* 1960). From this biochemical information it seems natural to expect the existence of substantial difference in the molecular structures of the tetra- and penta-peptide. In fact, the difference has already been suggested on the basis of their crystallographic data (Sasada, Tanaka, Ogawa & Kakudo, 1961; Sasada & Kakudo, 1961; Kakudo

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