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Metal Complexes with Mixed Ligands. 9. The Crystal Structure of Aquatrisimidazolecopper(II) Sulphate, $Cu(H_2O)(C_3H_4N_2)_3SO_4$

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The crystal structure of $Cu(H_2O)(C_3H_4N_2)_3SO_4$ has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic, spacegroup $P2_1/n$, with unit cell dimensions and corresponding standard deviations (at 25 °C) $a = 14.239(1)$ Å; $b = 8.707(1)$ Å; $c = 11.717(1)$ Å and $\beta = 90.244(5)°$. There are four formula units per unit cell. Intensities were collected and measured with the linear diffractometer PAILRED using Mo$K\alpha$ radiation. The structure was solved by routine heavy-atom methods and refined by full matrix least-squares methods. With positional coordinates of all atoms and anisotropic thermal factors of non-hydrogen atoms as parameters the structure was refined to a conventional R-value of 0.043. The refinement was based on 3032 observations. The distorted octahedron around copper is formed by four short bonds from three imidazole nitrogens and one sulphate oxygen and two longer bonds formed by one sulphate oxygen and the water oxygen. The sulphate group forms a bridge between copper atoms leading to infinite chains along the two-fold screw axes. Both within and between the chains there are hydrogen bonds between the nitrogens not coordinated to copper atoms, the sulphate oxygens, and the water oxygen.

The investigation of metal-imidazole-complexes forms the basis of a research programme at this department which aims at determining the different possible coordinations of the histidine residue imidazole to metal atoms as models for the more complex biological systems where metal atoms interact with histidine residues. The formation of Cu(II)-imidazole complexes with different anions have been studied especially, both in the crystalline state and in solution.[1-8]

When the ratio of imidazole to copper is varied, mononuclear complexes are formed in solution where the number of imidazole rings bound to Cu(II) varies from one to six. If the anion medium is varied, most of the complexes with a composition corresponding to these mononuclear species can crystallize. At this stage the crystal structures of Cu(II)-imidazole complexes with Cl^-, ClO_4^- and SO_4^{2-} have been determined.[2-4] They contain complexes with the ratio $C_3H_4N_2$:Cu = 2:1, 3:1, and 4:1. Two complexes have been crystallized with PO_4^{3-} as anion and the chemical analyses correspond to the formulas $Cu(C_3H_4N_2)_5HPO_4.5H_2O$ and $Cu(C_3H_4N_2)_6(H_2PO_4)_2.2H_2O$. The structure determinations of these are in progress and may possibly confirm the suggested 5:1 and 6:1 coordinations. In the sulphate medium two different species have so far been crystallized; the first was $Cu(C_3H_4N_2)_4SO_4$[3] and the other is $Cu(H_2O)(C_3H_4N_2)_3SO_4$ which is the subject of this communication.

EXPERIMENTAL

Crystal preparation and analysis. In a typical preparation of the crystals 30 ml of a 1 M imidazole solution were added to 10 ml of 1 M $CuSO_4$ solution and the pH of the mixture was adjusted to about 6.5 by adding 0.1 M sulphuric acid. The solution was left to evaporate at room temperature and after a few days blue crystals, in the shape of well-defined prisms, were formed. They were not stable in air. The copper content was determined by titration with EDTA,[9] and the nitrogen content was determined using the Kjeldahl method.[10] With the aid of IR-spectra the presence of H_2O was indicated. Using a thermal balance it could be shown that the crystals lose one water molecule per formula unit after heating to 130 – 140 °C. The following analyses (in weight-%) were obtained. Found: Cu 16.4; N 21.7; H_2O 4.6. Calc. for $Cu(H_2O)$-

$(C_3H_4N_2)_3SO_4$: Cu 16.6; N 22.0; H_2O 4.7. The density of the crystals was determined by flotation (using bromoform and xylene) to be 1.73 g/cm³. With four units of $Cu(H_2O)(C_3H_4N_2)_3SO_4$ in the unit cell the calculated density is 1.74 g/cm³.

Unit cell data and spacegroup. From rotation photographs around the *a*- and *b*-axes and corresponding Weissenberg photographs ($0kl-2kl$ and $h0l-h2l$) taken with Cu$K\alpha$-radiation, it was concluded that the crystals are monoclinic. The systematic extinctions for $h0l$ when $h+l$ is odd and for $0k0$ when k is odd are characteristic for the spacegroup $P2_1/n$ (No. 14).[11] The dimensions of the unit cell were determined with the aid of powder photographs taken with a camera of Guinier-Hägg type using 45 observations in a least-squares refinement. The following parameters and corresponding standard deviations were obtained: $a=14.239(1)$ Å; $b=8.707(1)$ Å; $c=11.717(1)$ Å; and $\beta=90.244(5)°$.

Collection and reduction of intensity data. The intensities were measured with an automatic linear diffractometer (PAILRED) using Mo$K\alpha$-radiation, graphite monochromator and pulse height discriminator. The specimen crystal was enclosed, together with part of the crystallization mother liquid, in a sealed capillary of Lindeman glass. It was mounted around the *b*-axis and about 4300 independent reflexions from ten reciprocal levels ($h0l-h9l$) were measured. All reflexions with counts less than 10 000 were measured up to three times; background radiation was measured for 40 s on each side of every reflexion. For the $h0l$ layer the half-scan ranges were 1.1° and 1.4° for $\theta \geq 22°$ (ω_1) and $\theta < 22°$(ω_2) respectively. The half-scan ranges were then gradually increased to the value of 1.3° and 1.8° for the $h9l$-layer. The scan speed used was 1 deg./min.

The intensities were corrected according to the relation $I=TI/N-\omega(B_1+B_2)/t_Bv$ where $I=$ net intensity, $TI=$ total intensity (peak + background), $N=$ number of scans over the reflexion, $\omega=$ the half-scan range, B_1 and $B_2=$ background intensities, $t_B=$ time for background measurement and $v=$ scan speed. The relative counting statistical error of each reflexion $\Delta I/I$ was calculated using the formula

$$\frac{\Delta I}{I} = \frac{[TI/N^2 + (\omega/t_Bv)^2(B_1+B_2) + (T^2/N^2) \times 0.0001]^{1/2}}{TI/N - [\omega(B_1+B_2)]/t_Bv}$$

where $(T^2/N^2) \times 0.0001$ is a term that corrects for the linear error in the diffractometer. Of 4300 measured reflexions 3032 were significant at the 95 % level, *i.e.* had $\Delta I/I < 0.50$. Lp and absorption corrections were then applied. The linear absorption coefficient is 17.29 cm^{-1} for Mo$K\alpha$-radiation; there was thus a variation in the transmission factors of 11 %.

The calculations were performed with a CDC 3300 computer using modified versions of the programmes mentioned by Ivarsson, Lundberg and Ingri.[4]

STRUCTURE DETERMINATION AND REFINEMENT

The position of the copper atom was found from the three-dimensional Patterson synthesis. Heavy atom Fourier methods allowed the determination of the approximate positions of the other non-hydrogen atoms. However, to distinguish N(2), N(4), and N(6) from C(2), C(5), and C(8) (see Fig. 1 for numbering) all six atoms were refined as carbons and then the group of three atoms with the lower temperature factors was labelled nitrogen prior to further refinement.

The atomic coordinates and anisotropic temperature factors were refined using full matrix least-squares techniques. The reflexions were weighted according to the method suggested by Cruickshank,[12] $\omega = 1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$ using constants $a=100$, $c=-0.02$, $d=0.0006$.

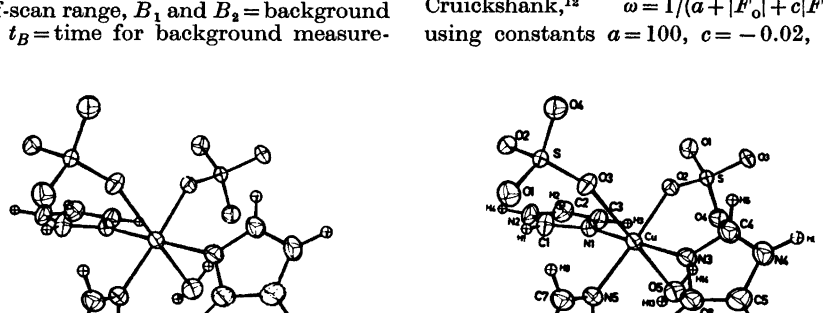

Fig. 1. A stereoscopic illustration of a molecule viewed along the *a*-axis. Thermal ellipsoids are scaled to enclose 50 % probability. The parenthesis around the numbers are omitted in the figure.

Table 1a. Fractional atomic coordinates and anisotropic thermal parameters. Their estimated standard deviations are given in parentheses. All values are multiplied by 10^4. Anisotropic temperature factors have been calculated according to the formula
$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2792(0.3)	1506(0.5)	746(0.3)	29(0.2)	59(1)	38(0.3)	−15(0.5)	−14(0.3)	22(1)
S	1079(1)	4198(1)	2495(1)	25(0.3)	49(1)	33(0.5)	2(1)	0(1)	−6(1)
01	4572(2)	−148(3)	3356(2)	32(1)	83(4)	63(2)	3(3)	−32(3)	−11(4)
02	3259(2)	423(3)	2158(2)	34(1)	68(3)	41(1)	12(3)	−10(2)	19(4)
03	1586(2)	2901(3)	2011(2)	40(1)	65(3)	46(2)	19(3)	6(2)	−30(4)
04	539(2)	3678(3)	3509(2)	46(1)	84(4)	51(2)	−2(4)	39(3)	−4(4)
05	3896(2)	113(4)	−513(2)	40(1)	117(5)	63(2)	4(4)	6(3)	−8(5)
N1	3734(2)	3159(3)	1056(2)	33(1)	52(4)	46(3)	−9(3)	2(3)	3(4)
N2	4344(3)	5417(4)	1367(3)	55(2)	62(5)	70(3)	−26(5)	13(4)	−33(5)
C1	3564(3)	4640(5)	1096(4)	38(2)	74(5)	72(3)	4(5)	9(4)	−5(6)
C2	5047(3)	4384(5)	1513(4)	37(2)	110(6)	67(3)	−28(5)	−3(4)	−20(7)
C3	4664(2)	2993(5)	1321(3)	33(2)	78(5)	59(3)	−3(4)	−6(3)	−16(6)
N3	1884(2)	−201(3)	441(2)	30(1)	74(4)	34(2)	−13(3)	−1(2)	12(4)
N4	1113(2)	−2372(4)	618(3)	42(2)	82(5)	60(2)	−39(4)	−5(3)	23(5)
C4	1748(3)	−1428(5)	1082(3)	38(2)	87(5)	51(2)	−35(5)	−7(3)	17(6)
C5	811(3)	−1711(5)	−379(3)	47(2)	119(7)	54(3)	−43(6)	−24(4)	−4(6)
C6	1290(3)	−392(5)	−484(3)	46(2)	100(6)	45(2)	−47(5)	−27(4)	16(6)
N5	2315(2)	2685(4)	−597(7)	29(1)	81(4)	40(2)	−7(4)	−2(2)	23(4)
N6	1374(2)	3980(4)	−1710(3)	41(2)	121(5)	50(2)	15(5)	−15(3)	39(5)
C7	1522(2)	3464(5)	−647(3)	34(2)	94(5)	44(2)	−14(5)	−11(3)	15(6)
C8	2101(3)	3506(6)	−2373(3)	53(2)	164(8)	44(3)	11(7)	4(4)	65(7)
C9	2689(3)	2707(5)	−1679(3)	36(2)	122(6)	53(3)	21(5)	15(3)	31(6)

Table 1b. Fractional atomic coordinates and isotropic thermal parameters for the hydrogen atoms. Their estimated standard deviations are given in parentheses. All coordinates are multiplied by 10^4.

	x	y	z	B(Å^2)
H1	2991(33)	5132(62)	951(43)	4.3(1.1)
H2	5655(40)	4678(75)	1655(51)	6.1(1.4)
H3	4935(31)	2016(58)	1287(39)	3.6(1.0)
H4	4413(35)	6335(62)	1446(44)	4.5(1.1)
H5	1998(35)	−1500(61)	1775(43)	4.6(1.2)
H6	336(35)	−2096(66)	−877(44)	4.9(1.2)
H7	1237(29)	379(53)	−1067(37)	3.2(0.9)
H8	906(33)	−3221(59)	980(41)	4.1(1.1)
H9	1151(33)	3743(57)	−2(40)	3.8(1.0)
H10	2142(38)	3762(67)	−3161(46)	5.3(1.3)
H11	3236(30)	2330(54)	−1840(37)	3.3(0.9)
H12	842(31)	4503(58)	−1914(39)	3.8(1.0)
H13	4451(38)	571(74)	−837(48)	5.8(1.4)
H14	4179(41)	−405(79)	23(53)	6.5(1.5)

The atomic scattering factors for Cu^{2+}, S, O, N, and C were taken from the International Tables.[14] Account was taken of the real part of the dispersion correction for Cu^{2+} and S. Refinement, not including hydrogen atoms, was terminated at an R-value $= (\sum||F_o|-|F_c||)/\sum|F_o| = 0.049$.

A difference Fourier map was then calculated and peaks on it could be postulated as being due to hydrogen atoms. Refinement including the hydrogen coordinates and their isotropic thermal parameters was made, using the scattering factors proposed by Stewart, Davidson and Simpson.[13] This was terminated when all param-

Table 2. Observed and calculated structure factors (× 10).

L	H			L	H			L	H			L	H			L	H			L	H		
				6-16	192	188		0	6	333	358	10	6	143	137	6	12	167	160	3	0	1250	1165	15	0	181	189
K=	0			6-14	157	161		0	4	528	554	10	5	141	133	6	10	242	238	3	1	1077	1005	15	-1	109	131
				6-12	330	330						10	4	311	315	6	9	641	641	3	2	561	546	15	-4	97	109
16	-2	83	94	6-10	478	471	K=	1				10	3	214	203	6	8	399	408	3	3	718	700	14	-7	154	158
16	0	158	148	6 -8	98	102						10	2	171	179	6	7	569	569	3	4	253	264	14	-2	91	78
16	4	142	132	6 -6	104	105	17	-2	82	80		10	1	404	405	6	6	314	320	3	6	610	631	14	-1	309	318
16	6	125	117	6 -4	548	528	17	2	77	114		10	0	119	132	6	5	105	100	3	7	260	282	14	0	148	149
15	9	112	109	6 -2	1285	1249	16	4	117	121		10	-2	402	416	6	4	242	229	3	8	187	190	14	1	329	337
15	7	144	140	6 0	1002	991	16	2	110	110		10	-4	240	239	6	2	184	168	3	9	789	783	14	3	76	48
15	5	224	245	6 2	874	824	16	1	138	137		10	-5	348	357	6	1	228	208	3	10	300	306	14	7	102	104
15	3	175	204	6 4	289	300	16	0	155	164		10	-6	98	96	6	0	104	111	3	11	372	381	14	8	76	85
15	1	156	170	6 6	633	641	16	-2	208	213		10	-7	143	145	6	-1	511	498	3	12	568	565	13	10	294	300
15	-3	142	148	6 8	560	549	16	-4	95	113		10	-9	107	104	6	-2	428	426	3	13	190	190	13	8	124	141
15	-7	191	211	6 10	390	384	16	-5	79	93		10	-11	98	95	6	-3	566	545	3	14	166	151	13	7	69	11
14	-10	75	80	6 14	94	96	16	-8	83	24		10	-12	115	98	6	-4	212	221	3	15	222	224	13	6	124	115
14	-4	376	396	6 16	217	215	15	-9	117	110		10	-14	146	147	6	-5	122	120	3	16	152	155	13	4	284	291
14	-2	212	229	6 18	242	221	15	-6	183	189		10	-15	187	186	6	-6	285	303	3	17	74	96	13	3	120	155
14	2	135	128	5 19	136	117	15	-4	172	174		9	-11	171	180	6	-7	124	116	2	20	173	166	13	0	190	192
14	4	218	226	5 17	98	89	15	-3	128	134		9	-10	70	75	6	-8	84	96	2	19	79	83	13	-2	109	112
14	8	143	138	5 15	61	44	15	-1	132	143		9	-9	298	308	6	-9	473	483	2	18	115	120	13	-3	86	108
13	13	194	180	5 13	123	101	15	0	80	88		9	-8	119	115	6	-10	210	218	2	17	142	136	13	-4	78	66
13	9	191	193	5 11	836	824	15	1	83	89		9	-7	339	361	6	-12	285	289	2	16	104	121	13	-6	187	184
13	7	427	434	5 9	582	581	15	4	96	76		9	-6	534	539	6	-14	74	63	2	15	174	183	13	-7	150	155
13	5	186	188	5 7	177	170	15	6	135	121		9	-5	154	144	6	-16	81	71	2	14	142	159	13	-8	227	236
13	1	102	103	5 5	462	442	15	9	131	131		9	-4	284	287	6	-18	68	40	2	13	250	241	13	-10	114	101
13	-1	95	89	5 3	450	419	14	11	90	60		9	-3	571	570	6	-19	105	100	2	12	176	173	12	-9	150	150
13	-3	305	297	5 -1	1014	993	14	10	136	140		9	-1	409	401	5	-18	70	61	2	11	179	184	12	-8	71	70
13	-5	317	317	5 -3	1030	1009	14	8	200	217		9	0	183	183	5	-17	95	91	2	10	139	142	12	-7	196	180
13	-11	172	158	5 -5	127	82	14	7	152	160		9	2	267	256	5	-16	135	152	2	8	530	533	12	-6	98	88
12	-14	102	99	5 -7	688	685	14	6	127	150		9	3	121	126	5	-15	168	160	2	7	139	147	12	-5	94	103
12	-12	284	278	5 -9	120	118	14	5	207	218		9	4	336	352	5	-14	143	146	2	5	265	289	12	-3	193	204
12	-10	159	149	5 -13	203	196	14	4	108	115		9	5	139	142	5	-13	395	401	2	4	442	450	12	-2	187	177
12	-8	102	93	5 -17	205	217	14	3	111	118		9	6	231	231	5	-12	158	148	2	3	441	438	12	-1	119	129
12	-6	67	67	5 -19	160	150	14	2	100	108		9	7	288	290	5	-11	505	522	2	2	1166	1127	12	1	96	104
12	-4	65	47	4 -20	68	41	14	0	69	21		9	9	322	320	5	-10	262	263	2	1	261	250	12	2	240	239
12	0	289	286	4 -18	82	88	14	-1	71	91		9	10	181	173	5	-9	158	160	2	0	319	268	12	3	373	384
12	2	273	276	4 -14	569	565	14	-3	138	128		9	11	161	137	5	-8	299	298	2	-1	1197	1112	12	4	166	174
12	4	368	376	4 -12	650	650	14	-5	206	209		9	12	316	305	5	-7	343	341	2	-2	868	851	12	5	224	223
12	6	580	570	4 -10	151	162	14	-7	82	44		9	13	152	147	5	-6	408	387	2	-3	1517	1512	12	6	72	77
12	8	282	276	4 -8	536	539	14	-8	151	129		9	14	149	140	5	-5	169	172	2	-4	287	308	12	7	89	84
11	13	164	166	4 -6	765	770	14	-10	155	152		9	15	166	166	5	-4	182	181	2	-5	191	200	12	9	147	158
11	11	370	370	4 -2	583	541	14	-11	81	83		9	17	134	121	5	-2	197	177	2	-6	114	100	12	11	123	126
11	9	359	369	4 0	612	566	13	-12	155	145		8	18	115	108	5	-1	217	231	2	-7	316	317	11	13	111	114
11	7	87	77	4 2	119	103	13	-11	76	64		8	17	164	153	5	0	188	186	2	-8	251	250	11	12	170	176
11	5	240	249	4 4	1258	1260	13	-9	160	175		8	14	93	73	5	1	233	233	2	-9	332	346	11	9	134	139
11	3	195	201	4 6	611	628	13	-5	113	125		8	13	187	193	5	2	616	588	2	-10	373	379	11	7	119	115
11	1	237	227	4 8	381	381	13	-3	199	206		8	12	116	98	5	3	710	687	2	-11	256	259	11	6	170	158
11	-1	114	99	4 10	1058	1042	13	-2	204	207		8	11	220	221	5	4	481	477	2	-12	196	184	11	4	214	211
11	-3	180	188	4 12	477	466	13	-1	171	174		8	10	302	298	5	5	974	981	2	-13	305	308	11	3	73	70
11	-5	448	463	4 14	77	44	13	1	286	307		8	9	80	71	5	7	786	791	2	-14	189	179	11	2	454	463
11	-7	384	391	4 20	112	106	13	3	245	247		8	8	632	628	5	8	422	441	2	-15	71	75	11	1	88	98
11	-9	85	80	3 19	159	156	13	4	258	267		8	7	111	107	5	9	270	281	2	-16	213	201	11	0	244	249
11	-11	152	150	3 17	135	126	13	5	145	139		8	6	313	311	5	10	187	176	2	-19	110	101	11	-1	66	39
10	-14	189	188	3 15	232	229	13	6	141	142		8	5	569	565	5	11	178	183	1	-21	138	110	11	-2	425	438
10	-8	354	358	3 13	506	510	13	7	118	128		8	4	170	171	5	12	82	72	1	-20	168	164	11	-3	129	119
10	-6	477	495	3 9	75	52	13	13	107	83		8	3	187	179	5	13	78	48	1	-18	154	146	11	-4	283	278
10	-4	305	314	3 7	378	381	12	14	135	125		8	2	499	506	5	15	75	73	1	-17	213	206	11	-10	139	153
10	-2	107	122	3 5	676	664	12	12	218	214		8	1	307	299	5	19	107	78	1	-16	154	156	11	-14	177	170
10	0	553	553	3 3	1301	1292	12	11	142	133		8	0	451	449	5	20	127	106	1	-15	281	281	10	-13	78	63
10	2	187	201	3 1	85	74	12	10	168	172		8	-1	165	157	4	20	101	71	1	-13	148	149	10	-12	131	124
10	4	468	474	3 -1	1388	1290	12	9	191	194		8	-2	148	148	4	19	82	101	1	-12	268	271	10	-11	283	282
10	8	187	193	3 -3	839	831	12	8	162	168		8	-4	66	62	4	17	79	75	1	-11	76	72	10	-10	112	113
10	10	462	457	3 -5	809	806	12	7	154	150		8	-5	195	178	4	16	222	221	1	-10	145	149	10	-9	324	327
10	12	379	359	3 -7	114	125	12	6	211	215		8	-6	86	108	4	14	325	322	1	-9	583	570	10	-7	226	225
9	17	74	52	3 -9	125	128	12	5	81	76		8	-7	88	83	4	13	222	218	1	-8	74	100	10	-6	143	139
9	15	213	211	3 -11	207	198	12	3	75	20		8	-8	421	421	4	12	233	230	1	-7	287	302	10	-5	184	186
9	9	207	208	3 -13	422	420	12	2	160	167		8	-10	145	135	4	11	284	284	1	-6	479	479	10	-4	294	288
9	7	312	312	3 -15	324	318	12	1	68	67		8	-11	225	246	4	10	409	425	1	-5	900	809	10	-3	287	288
9	5	336	339	3 -17	79	56	12	-1	389	400		8	-12	87	99	4	9	92	79	1	-4	119	112	10	-2	144	153
9	3	532	530	2 -20	138	129	12	-3	260	268		8	-13	204	196	4	8	205	205	1	-3	1379	1386	10	-1	95	98
9	1	188	180	2 -16	141	133	12	-4	335	338		8	-14	84	79	4	7	419	415	1	3	742	744	10	0	254	253
9	-1	496	506	2 -14	225	221	12	-6	196	186		8	-16	104	109	4	6	443	437	1	4	302	295	10	1	202	196
9	-3	714	720	2 -12	402	399	12	-7	90	88		8	-18	72	51	4	5	221	203	1	5	302	294	10	3	71	80
9	-5	141	141	2 -10	457	445	12	-8	79	78		7	-18	84	85	4	4	193	208	1	7	84	76	10	4	84	96
9	-7	314	305	2 -8	456	464	12	-9	172	172		7	-17	151	142	4	3	1103	1081	1	8	264	272	10	5	337	332
9	-9	189	189	2 -6	825	823	12	-12	156	151		7	-16	78	60	4	1	814	769	1	10	455	470	10	6	120	120
9	-13	232	230	2 -4	456	455	12	-13	103	112		7	-15	180	177	4	0	458	431	1	11	313	316	10	7	539	547
9	-15	288	282	2 -2	1533	1488	11	-13	245	233		7	-12	294	288	4	-1	311	326	1	13	324	324	10	8	97	87
8	-16	97	91	2 0	203	199	11	-11	126	125		7	-11	143	134	4	-2	881	871	1	14	80	75	10	9	307	318
8	-14	169	163	2 2	272	258	11	-10	184	196		7	-9	116	107	4	-3	356	358	1	15	206	197	10	11	142	142
8	-10	348	353	2 4	131	128	11	-9	121	118		7	-8	306	305	4	-4	921	897	1	16	288	284	10	13	154	142
8	-8	291	296	2 8	248	259	11	-8	185	185		7	-7	75	67	4	-5	786	792	1	17	131	136	10	14	114	106
8	-6	281	288	2 10	603	582	11	-7	76	76		7	-6	158	175	4	-6	468	458	1	18	72	58	10	15	114	109
8	-4	803	786	2 12	677	676	11	-5	214	218		7	-5	441	454	4	-7	60	36	1	19	158	145	10	16	90	88
8	-2	859	864	2 14	403	395	11	-4	216	219		7	-4	234	233	4	-8	211	211	0	21	86	60	9	16	200	195
8	0	542	525	2 20	108	100	11	-3	158	161		7	-3	606	583	4	-9	279	275	0	19	185	179	9	10	97	97
8	2	567	579	1 19	198	170	11	-2	188	189		7	-2	441	434	4	-10	203	205	0	18	82	57	9	9	259	251
8	6	288	288	1 17	245	235	11	-1	150	159		7	-1	846	813	4	-11	156	154	0	15	300	300	9	8	289	280
8	8	221	217	1 15	176	170	11	0	78	90		7	0	783	757	4	-12	292	302	0	14	102	101	9	7	174	171
8	10	181	168	1 13	263	251	11	1	166	159		7	1	651	633	4	-14	182	175	0	13	73	67	9	6	217	215
8	12	145	145	1 11	258	262	11	2	263	257		7	2	88	75	4	-15	201	198	0	12	148	140	9	5	239	251
8	14	323	321	1 9	540	547	11	3	181	183		7	3	428	415	4	-17	195	187	0	11	290	297	9	4	265	262
8	16	250	231	1 7	342	385	11	4	179	175		7	4	150	150	4	-18	104	87	0	10	422	430	9	3	91	99
7	19	134	114	1 5	597	588	11	5	327	324		7	6	294	300	4	-20	128	116	0	9	458	479	9	2	443	446
7	17	73	46	1 3	1222	1244	11	6	178	189		7	8	275	277	3	-19	93	90	0	8	559	580	9	1	330	334
7	15	104	102	1 -3	588	563	11	7	307	297		7	10	177	169	3	-16	141	136	0	7	458	475	9	0	618	609
7	13	141	128	1 -5	404	410	11	8	224	230		7	11	79	62	3	-15	207	214	0	6	501	526	9	-1	256	256
7	11	96	83	1 -7	906	895	11	9	153	157		7	12	76	77	3	-14	64	15	0	4	387	389	9	-3	180	173
7	9	508	502	1 -9	655	654	11	10	214	210		7	13	262	267	3	-13	92	73	0	3	572	590	9	-5	221	203
7	7	1028	1006	1 -11	603	598	11	11	165	168		7	14	74	81	3	-12	286	292					9	-6	214	224
7	5	188	207	1 -13	152	148	11	13	106	126		7	15	199	196	3	-11	348	356	K=	2			9	-7	74	78
7	1	344	333	1 -15	77	82	10	16	140	156		7	16	171	159	3	-10	259	251					9	-9	78	63
7	-1	918	875	1 -17	276	263	10	15	89	59		7	17	142	141	3	-9	478	506	16	-5	141	145	9	-10	337	347
7	-3	719	736	0 20	115	89	10	14	109	116		7	18	104	86	3	-8	438	431	16	-4	85	80	9	-11	83	89
7	-5	570	553	0 18	337	328	10	13	241	245		7	19	163	166	3	-7	163	180	16	-3	184	196	9	-12	256	258
7	-7	171	163	0 16	232	225	10	12	113	95		6	19	144	110	3	-6	756	760	16	1	78	58	8	-16	97	83
7	-9	250	249	0 14	76	55	10	10	171	177		6	17	73	80	3	-5	665	638	15	8	134	134	8	-12	164	162
7	-11	307	307	0 12	397	410	10	9	195	197		6	15	170	172	3	-3	1152	1117	15	6	141	146	8	-11	191	194
7	-15	79	43	0 10	121	131	10	8	117	112		6	14	116	109	3	-2	1199	1194	15	5	95	77	8	-10	156	151
6	-18	231	217	0 8	284	279	10	7	177	184		6	13	125	130	3	-1	396	382	15	2	154	166	8	-8	317	324

Table 2. Continued.

L	H			L	H			L	H			L	H			L	H			L	H		
					4-15	92	76	1	5	229	252	11	-6	234	237	6	-8	121	126	3-12	239	246	13	10	109	82
K=	2				4-13	75	76	1	4	1242	1275	11	-7	84	90	6	-7	807	812	3-13	67	68	13	9	109	79
					4-12	223	225	1	3	82	50	11	-8	192	200	6	-6	630	627	3-14	67	39	13	8	150	145
8	-7	391	395		4-11	525	537	1	2	1642	1706	11	-10	207	206	6	-5	649	635	3-19	144	144	13	7	141	153
8	-6	159	162		4-10	223	230	1	-2	146	125	11	-12	127	129	6	-4	291	288	2-19	118	103	13	6	129	144
8	-5	425	447		4	-9	675	673	1	-3	89	57	11	-13	152	154	6	-3	366	365	2-17	214	214	13	1	74	72
8	-3	313	327		4	-8	89	110	1	-4	210	189	10	-13	70	59	6	-1	158	97	2-16	157	159	13	0	173	171
8	-1	756	736		4	-7	134	139	1	-5	741	731	10	-12	149	148	6	0	335	315	2-15	224	223	13	-3	113	104
8	0	332	319		4	-6	155	159	1	-6	447	466	10	-11	101	83	6	2	109	100	2-13	337	341	13	-4	169	182
8	1	276	277		4	-5	389	402	1	-7	98	80	10	-3	138	156	6	3	154	143	2-11	293	287	13	-5	144	155
8	2	366	362		4	-4	791	769	1	-8	628	661	10	-2	399	405	6	4	174	157	2-10	471	484	13	-6	85	24
8	6	237	250		4	-3	64	74	1	-9	101	96	10	-1	398	405	6	5	440	453	2	-9	134	134	13	-7	139	136
8	7	72	58		4	-2	230	230	1-10		220	238	10	0	200	203	6	6	311	315	2	-8	200	206	13	-9	114	108
8	9	234	225		4	-1	224	237	1-11		193	199	10	1	490	502	6	7	201	194	2	-7	147	158	13-10		180	162
8	10	222	220		4	0	333	321	1-12		315	313	10	2	170	180	6	8	77	79	2	-6	64	72	13-11		74	100
8	11	414	411		4	1	368	349	1-14		524	521	10	3	347	347	6	9	188	179	2	-4	503	474	12-12		105	98
8	12	87	83		4	2	759	720	1-15		90	96	10	4	304	310	6	11	610	619	2	-3	47	32	12-11		104	98
8	13	203	202		4	3	194	193	1-16		124	120	10	5	332	339	6	12	369	372	2	-1	1058	991	12-10		151	139
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7	16	72	41		4	6	382	311	0	2	844	853	10	12	88	82	6	16	87	91	2	2	864	878	12	-4	117	118
7	15	130	124		4	7	1004	1031	0	3	1477	1510	10	13	141	136	6	18	101	84	2	3	537	538	12	-1	257	257
7	12	292	284		4	8	389	401	0	4	670	707	10	15	203	193	5	18	157	153	2	4	254	267	12	0	315	333
7	11	115	108		4	9	314	331	0	5	754	778	9	15	119	119	5	17	158	153	2	5	1090	1119	12	1	249	250
7	10	389	394		4	10	160	168	0	6	261	253	9	14	185	163	5	16	86	89	2	6	155	149	12	2	302	312
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7	8	129	142		4	13	169	150	0	9	222	213	9	11	83	99	5	11	75	61	2	8	524	534	12	4	74	72
7	7	68	74		4	14	341	349	0	10	142	153	9	10	338	344	5	10	190	195	2	9	238	249	12	5	81	62
7	6	456	449		4	17	115	107	0	13	215	212	9	9	101	124	5	9	386	393	2	10	177	194	12	6	144	140
7	5	390	391		4	19	107	107	0	14	191	192	9	8	331	334	5	8	245	253	2	11	167	167	12	7	158	154
7	4	987	949		3	19	120	114	0	15	298	302	9	6	183	172	5	7	369	363	2	12	67	71	12	8	171	164
7	3	180	186		3	18	250	239	0	16	177	176	9	5	102	86	5	6	363	375	2	13	172	181	12	9	139	133
7	2	555	536		3	17	105	111	0	17	93	91	9	3	304	290	5	5	510	500	2	14	88	77	11	12	74	74
7	1	196	192		3	16	266	258	0	19	149	138	9	1	303	295	5	4	425	443	2	15	75	78	11	11	139	126
7	0	377	355		3	14	181	178	0	20	107	98	9	0	189	190	5	3	101	93	2	17	179	181	11	10	140	145
7	-1	190	172		3	13	89	105					9	-1	304	292	5	2	948	910	2	18	91	93	11	9	102	97
7	-2	375	356		3	12	129	120	K=	3			9	-3	87	77	5	1	152	144	2	19	97	96	11	8	84	84
7	-3	482	462		3	11	561	576					9	-4	494	502	5	0	695	657	1	19	100	75	11	5	97	103
7	-4	78	56		3	10	107	94	16	-2	121	128	9	-5	212	213	5	-1	359	334	1	18	147	141	11	4	79	73
7	-5	224	210		3	9	153	156	16	1	111	120	9	-6	343	353	5	-2	534	498	1	16	180	184	11	3	189	205
7	-6	555	563		3	8	448	452	16	3	172	179	9	-7	96	104	5	-3	378	364	1	14	359	364	11	1	285	290
7	-7	367	369		3	7	255	268	15	5	84	85	9	-8	189	176	5	-4	62	69	1	13	351	364	11	0	473	467
7	-8	530	529		3	6	797	788	15	2	93	90	9	-9	98	107	5	-5	455	448	1	12	309	324	11	-1	308	311
7	-9	128	129		3	5	164	172	15	1	74	78	9	-10	261	266	5	-6	361	353	1	11	188	185	11	-2	260	263
7	-10	213	218		3	4	67	70	15	0	107	87	9	-13	91	94	5	-7	220	217	1	10	129	127	11	-3	149	148
7	-11	64	61		3	2	663	633	15	-1	129	122	8	-15	59	59	5	-8	371	382	1	9	170	167	11	-5	191	190
7	-12	215	213		3	1	324	312	15	-2	157	176	8	-16	116	105	5	-9	432	435	1	8	532	557	11	-6	173	170
7	-13	96	91		3	0	950	892	15	-3	131	124	8	-15	193	192	5	-10	292	294	1	7	326	327	11	-7	166	181
7	-14	224	223		3	-1	625	608	15	-4	129	125	8	-13	142	135	5	-11	97	103	1	6	249	233	11	-8	89	107
7	-15	90	88		3	-2	559	539	15	-6	162	156	8	-11	240	234	5	-13	133	137	1	5	878	922	11	-10	87	79
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7	-18	73	71		3	-4	468	445	14	-10	102	92	8	-9	301	301	5	-16	137	142	1	3	481	481	10	-12	102	103
6	-17	90	80		3	-5	332	322	14	-9	123	116	8	-8	337	345	5	-17	85	62	1	2	322	341	10	-10	196	196
6	-15	211	221		3	-6	383	398	14	-8	149	151	8	-7	79	78	5	-18	109	97	1	-2	226	257	10	-9	131	132
6	-14	146	133		3	-7	551	563	14	-7	191	192	8	-5	231	236	5	-19	72	42	1	-3	391	377	10	-8	114	107
6	-13	262	266		3	-8	75	72	14	-2	177	160	8	-2	309	293	4	-19	182	172	1	-4	894	897	10	-7	288	279
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6	-11	81	58		3	-10	345	358	14	2	78	119	8	0	79	92	4	-17	193	178	1	-6	607	611	10	-5	75	76
6	-10	83	76		3	-11	186	186	14	3	146	145	8	1	277	273	4	-15	227	224	1	-8	127	132	10	-4	113	100
6	-9	73	53		3	-12	239	247	14	5	184	178	8	2	371	360	4	-14	84	99	1	-9	259	249	10	-2	179	176
6	-8	290	296		3	-13	65	57	14	6	98	75	8	3	778	798	4	-12	316	320	1	-11	62	79	10	-1	276	281
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6	-6	112	94		3	-15	183	192	14	9	135	129	8	5	500	499	4	-9	123	128	1	-13	221	226	10	3	321	319
6	-5	274	268		3	-16	268	269	14	10	93	89	8	6	74	67	4	-8	443	429	1	-14	149	152	10	4	227	228
6	-4	357	361		3	-17	132	127	13	9	74	48	8	7	233	236	4	-7	441	453	1	-15	171	162	10	5	366	360
6	-3	538	533		3	-18	203	191	13	8	113	98	8	8	150	158	4	-6	179	171	1	-16	191	202	10	6	186	188
6	-2	59	59		3	-19	97	82	13	6	131	125	8	9	87	85	4	-5	148	115	1	-17	143	132	10	7	119	122
6	-1	312	305		2	-19	160	124	13	5	105	91	8	10	167	167	4	-3	570	560	1	-18	146	151	10	8	138	136
6	0	268	257		2	-18	124	118	13	4	139	150	8	11	187	170	4	-2	298	301	1	-19	80	69	10	9	152	155
6	1	529	514		2	-17	188	185	13	3	116	125	8	12	88	91	4	-1	1026	996	0	2	480	520	10	10	210	215
6	3	713	699		2	-15	107	102	13	2	229	227	8	13	91	99	4	0	504	465	0	3	698	706	10	11	193	207
6	4	329	331		2	-14	64	70	13	1	194	189	8	15	125	99	4	1	849	805	0	4	995	1020	10	12	148	123
6	5	755	742		2	-11	231	234	13	0	283	291	8	16	87	81	4	2	193	168	0	5	824	873	10	14	118	103
6	6	185	190		2	-10	170	193	13	-2	77	90	7	16	204	189	4	3	656	630	0	6	369	385	9	14	117	102
6	8	208	220		2	-9	307	310	13	-4	119	133	7	14	212	197	4	4	115	108	0	7	508	550	9	13	151	153
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6	10	86	89		2	-7	1058	1054	12-12		103	86	7	12	313	321	4	7	63	70	0	9	399	419	9	7	182	190
6	11	143	135		2	-6	753	728	12-10		80	84	7	11	167	167	4	8	175	180	0	10	136	150	9	6	134	129
6	13	301	300		2	-5	1011	1018	12	-9	163	160	7	10	282	298	4	11	143	142	0	11	442	455	9	5	507	511
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7	11	278	291
7	10	113	122
7	9	343	339
7	8	314	324
7	7	223	215
7	6	342	349
7	5	208	206
7	3	251	237
7	2	18	18
7	-1	179	187
7	-5	186	187
7	-6	150	146
7	-7	307	310
7	-9	281	284
7-10		74	88
7-11		96	73
7-12		197	204
7-13		167	169
6-14		277	300
6-15		151	155
6-12		102	86
6-11		187	200
6-10		61	72
6	-9	150	150
6	-8	74	88
6	-7	122	123
6	-6	100	114
6	-5	195	192
6	-4	340	336
6	-3	220	222
6	-2	461	448
6	-1	324	312
6	0	204	206
6	1	184	181
6	2	517	500
6	3	87	90
6	4	407	410
6	7	340	372
6	8	83	85
6	9	158	160
6	10	74	61
6	13	100	97
6	14	240	234
6	15	113	105
5	15	203	215
5	14	140	133
5	13	217	219
5	12	94	111
5	11	71	95
5	10	142	147
5	9	294	309
5	8	86	73
5	7	400	406
5	6	85	89
5	4	177	171
5	3	570	563
5	2	77	78
5	1	198	174
5	0	276	265
5	-1	77	73
5	-2	507	486
5	-3	827	804
5	-4	352	363
5	-5	384	384
5	-6	273	271
5	-8	187	181
5	-9	196	204
5	-11	315	318

Table 2. Continued.

L	H		
K=	6		
5	-13	64	59
5	-15	99	103
4	-16	80	49
4	-15	105	103
4	-13	127	127
4	-12	296	299
4	-11	308	318
4	-10	321	314
4	-7	174	172
4	-5	207	222
4	-4	310	297
4	-3	147	209
4	-2	202	196
4	-1	219	215
4	0	462	430
4	1	359	345
4	2	267	263
4	3	512	495
4	4	56	21
4	5	188	196
4	6	339	341
4	7	179	184
4	8	319	329
4	9	216	219
4	10	149	169
4	11	181	176
4	12	74	83
4	13	66	78
4	14	160	185
4	16	81	51
3	14	87	70
3	11	190	201
3	10	204	219
3	9	63	81
3	7	283	307
3	6	158	171
3	5	342	342
3	3	244	251
3	2	316	317
3	1	761	735
3	0	350	333
3	-1	710	667
3	-2	203	193
3	-3	375	373
3	-4	209	211
3	-5	115	118
3	-6	186	180
3	-7	117	140
3	-8	76	84
3	-9	137	140
3	-11	255	273
3	-12	171	185
3	-13	76	85
3	-14	69	82
3	-15	82	104
3	-16	92	99
2	-14	121	131
2	-12	112	122
2	-10	64	55
2	-9	228	238
2	-8	433	446
2	-6	378	373
2	-5	289	289
2	-3	349	345
2	-2	365	368
2	-1	312	311
2	0	694	677
2	1	387	374
2	3	71	75
2	4	371	388
2	5	103	98
2	8	106	104
2	9	364	394
2	10	475	489
2	11	203	197
2	12	231	241
2	13	127	143
2	14	66	72
1	16	108	119
1	11	415	436
1	10	161	165
1	9	557	570
1	8	283	303
1	6	63	63
1	5	375	382
1	4	253	263
1	3	627	665
1	2	70	77
1	-2	92	95
1	-3	146	132
1	-4	319	315
1	-5	143	150
1	-6	195	196
1	-7	499	503
1	-8	66	60
1	-9	282	303
1	-10	235	251
1	-11	181	198
1	-12	222	240
1	-13	251	248
1	-14	102	135
1	-15	164	178
0	2	400	418
0	3	275	292
0	4	421	438
0	5	97	99
0	7	190	182
0	8	264	271
0	9	129	124
0	10	95	106
0	11	211	211
0	12	154	147
0	13	102	121
0	14	219	219
0	15	138	127
0	16	112	108
0	17	102	101
K=	7		
13	-4	156	170
13	-1	108	113
13	0	82	93
13	2	174	181
13	4	108	112
13	5	100	114
12	8	92	86
12	7	141	129
12	6	77	33
12	5	180	161
12	1	125	123
12	-1	91	63
12	-3	124	138
12	-5	332	336
12	-7	120	108
11	-7	76	54
11	-6	249	248
11	-4	150	136
11	-2	121	135
11	-1	93	92
11	1	67	74
11	2	122	123
11	4	209	215
11	6	261	262
11	7	133	109
10	9	147	151
10	8	95	77
10	6	82	43
10	5	219	222
10	3	175	175
10	2	104	113
10	1	172	177
10	0	90	92
10	-1	153	161
10	-3	227	224
10	-4	141	141
10	-5	87	83
10	-6	111	120
10	-7	78	61
10	-9	101	110
10	-11	76	83
9	-10	145	141
9	-8	347	342
9	-7	75	75
9	-6	134	140
9	-5	148	141
9	-4	285	281
9	-2	339	341
9	-1	143	135
9	0	160	160
9	1	123	112
9	7	73	89
9	8	322	319
9	10	299	307
9	11	104	90
8	12	98	89
8	9	334	332
8	7	206	207
8	6	100	104
8	5	73	58
8	4	75	101
8	3	367	352
8	2	122	124
8	1	411	398
8	0	96	109
8	-1	90	75
8	-2	211	205
8	-3	86	86
8	-4	67	63
8	-5	91	89
8	-6	144	148
8	-7	78	70
8	-9	266	279
8	-11	107	102
8	-12	91	86
7	-12	69	19
7	-11	94	91
7	-10	104	92
7	-9	120	102
7	-6	212	203
7	-5	149	157
7	-4	301	293
7	-3	204	193
7	-2	236	233
7	-1	377	370
7	0	264	257
7	1	61	55
7	2	514	506
7	3	108	98
7	4	84	93
7	5	135	123
7	6	83	66
7	7	95	100
7	8	112	99
7	9	163	158
7	11	73	75
7	12	225	224
7	14	116	126
6	13	266	269
6	11	221	222
6	10	123	128
6	9	140	134
6	8	171	167
6	7	238	238
6	5	379	374
6	2	114	112
6	1	261	262
6	-2	198	197
6	-3	380	374
6	-5	265	256
6	-6	139	139
6	-7	163	168
6	-8	123	115
6	-9	116	106
6	-10	121	119
6	-11	172	175
6	-12	104	94
6	-13	133	123
6	-15	117	125
5	-14	179	176
5	-13	102	74
5	-12	326	331
5	-10	182	176
5	-9	140	133
5	-8	203	215
5	-6	194	197
5	-5	72	79
5	-4	82	74
5	-3	82	82
5	-2	474	461
5	-1	143	143
5	0	285	276
5	1	202	204
5	3	106	122
5	4	539	537
5	5	79	80
5	6	426	434
5	7	215	214
5	8	180	187
5	9	65	72
5	11	72	53
5	12	128	124
5	13	107	100
4	15	233	233
4	14	70	76
4	13	119	98
4	12	150	148
4	11	147	144
4	10	146	141
4	9	199	200
4	8	179	185
4	7	118	120
4	6	185	190
4	5	271	276
4	3	332	328
4	2	165	156
4	0	65	61
4	-1	721	696
4	-3	439	426
4	-4	139	132
4	-6	221	222
4	-7	62	67
4	-8	110	98
4	-9	171	168
4	-10	106	106
4	-13	180	188
4	-14	87	74
4	-16	98	78
3	-16	112	107
3	-15	82	56
3	-14	111	99
3	-13	85	70
3	-11	153	154
3	-10	272	285
3	-8	454	448
3	-7	135	130
3	-6	323	322
3	-5	228	233
3	-4	186	190
3	-3	68	62
3	-2	508	496
3	-1	160	161
3	0	69	64
3	2	292	291
3	5	194	211
3	6	135	138
3	7	79	102
3	8	491	513
3	10	412	431
3	11	132	136
3	12	165	164
3	13	117	115
3	14	103	87
3	16	124	126
2	13	117	125
2	10	137	151
2	9	262	275
2	8	247	262
2	6	168	175
2	4	64	60
2	3	603	606
2	2	98	114
2	1	700	669
2	-1	159	169
2	-2	142	141
2	-3	112	125
2	-5	229	231
2	-6	135	146
2	-7	122	128
2	-8	95	103
2	-9	353	347
2	-11	88	76
2	-12	176	191
2	-13	102	115
2	-15	224	228
1	-16	141	159
1	-14	135	129
1	-12	100	99
1	-11	65	64
1	-9	222	228
1	-7	55	51
1	-6	529	541
1	-5	57	65
1	-4	275	268
1	-3	159	157
1	-2	194	204
1	2	616	625
1	3	130	151
1	4	347	376
1	5	80	93
1	6	211	221
1	10	194	196
1	12	328	323
1	14	113	103
1	15	86	86
0	13	173	173
0	11	373	384
0	10	186	186
0	9	240	244
0	8	131	131
0	7	380	391
0	5	413	430
0	4	192	197
0	3	73	87
0	2	373	391
K=	8		
12	-1	162	160
12	1	207	200
11	2	175	184
11	0	218	221
11	-3	68	53
11	-5	101	101
10	-7	289	283
10	-5	136	137
10	-4	102	103
10	-2	149	134
10	-1	68	57
10	3	175	167
10	5	108	114
10	8	72	61
9	7	120	118
9	4	260	260
9	3	70	44
9	2	340	335
9	1	95	94
9	0	123	112
9	-2	172	176
9	-3	138	131
9	-4	159	156
9	-6	93	85
8	-9	148	142
8	-8	155	158
8	-7	139	129
8	-6	136	142
8	-5	210	199
8	-3	383	376
8	-1	190	187
8	0	305	301
8	1	206	202
8	2	59	42
8	3	245	247
8	6	73	65
8	7	161	153
8	9	130	120
8	10	102	110
7	10	76	50
7	9	96	68
7	8	247	245
7	6	305	300
7	4	288	278
7	3	146	148
7	2	159	160
7	1	65	84
7	-1	212	198
7	-1	159	157
7	-2	66	71
7	-3	166	163
7	-4	215	213
7	-5	69	74
7	-7	104	100
7	-8	128	121
7	-10	252	247
7	-11	94	92
6	-11	206	211
6	-10	68	86
6	-9	126	135
6	-8	66	56
6	-7	123	114
6	-6	117	117
6	-5	56	54
6	-4	113	101
6	-2	100	102
6	-1	397	369
6	0	71	70
6	1	243	235
6	2	152	136
6	3	174	169
6	4	213	214
6	5	383	382
6	7	291	291
6	10	72	42
6	11	157	153
6	12	85	92
5	12	214	225
5	10	220	213
5	7	108	124
5	5	93	74
5	4	209	207
5	3	179	184
5	2	121	108
5	1	75	72
5	0	512	490
5	-2	276	261
5	-3	149	143
5	-4	101	88
5	-5	85	75
5	-6	295	287
5	-8	252	251
5	-13	73	74
4	-13	254	248
4	-12	71	66
4	-11	127	123
4	-10	95	89
4	-9	246	247
4	-8	89	104
4	-7	380	381
4	-6	119	123
4	-5	171	164
4	-4	184	169
4	-3	85	69
4	-2	115	117
4	-1	59	51
4	0	100	97
4	1	69	70
4	2	94	88
4	3	389	379
4	5	551	563
4	6	256	271
4	7	269	283
4	8	67	45
4	9	239	245
4	10	61	11
4	11	192	197
4	12	81	74
3	12	90	66
3	11	99	81
3	10	92	84
3	9	75	69
3	6	60	47
3	4	487	480
3	2	323	314
3	1	335	321
3	0	85	75
3	-1	103	102
3	-2	148	130
3	-4	285	276
3	-5	68	59
3	-6	254	255
3	-7	52	56
3	-9	145	154
3	-11	99	101
3	-12	131	130
3	-14	204	209
2	-14	93	94
2	-13	85	87
2	-11	102	107
2	-10	126	141
2	-9	163	154
2	-8	140	149
2	-7	340	334
2	-6	157	154
2	-5	438	626
2	-3	446	434
2	-1	56	57
2	0	293	280
2	1	80	84
2	2	209	219
2	3	279	282
2	4	180	182
2	6	103	87
2	7	302	314
2	9	131	138
2	10	166	162
2	11	165	169
2	12	77	82
2	13	177	182
1	12	87	81
1	11	66	69
1	8	263	271
1	6	450	441
1	5	146	159
1	4	136	143
1	3	145	139
1	2	339	350
1	-2	69	76
1	-3	103	94
1	-4	268	274
1	-5	116	106
1	-6	214	221
1	-7	286	295
L'	H		
1	-8	185	190
1	-9	80	73
1	-10	277	284
1	-11	63	29
1	-12	129	130
1	-13	83	110
0	2	170	146
0	3	193	197
0	4	202	227
0	5	227	220
0	7	302	309
0	8	120	134
0	10	73	50
0	11	155	162
0	12	93	91
K=	9		
11	-5	97	89
11	0	94	86
11	1	90	102
11	2	111	114
11	3	100	98
11	4	94	97
10	6	86	70
10	5	77	69
10	4	90	89
10	3	107	106
10	2	204	199
10	1	82	83
10	0	169	160
10	-1	91	90
10	-4	128	129
10	-5	74	97
10	-6	183	177
10	-7	99	95
10	-8	150	149
9	-8	167	161
9	-7	129	127
9	-6	200	199
9	-5	277	274
9	-4	90	102
9	-3	77	78
9	-1	80	84
9	1	90	82
9	5	125	124
9	7	91	78
8	8	66	5
8	7	85	85
8	6	257	256
8	5	89	113
8	4	220	223
8	3	145	139
8	2	60	66
8	1	175	169
8	0	107	107
8	-1	173	165
8	-2	60	55
8	-3	81	83
8	-5	64	25
8	-6	188	183
8	-7	101	82
8	-8	87	87
8	-9	74	54
8	-10	73	83
7	-9	88	78
7	7	87	92
7	-4	139	135
7	-3	194	187
7	-2	132	106
7	-1	360	354
7	0	200	191
7	1	105	111
7	2	204	197
7	3	105	99
7	4	130	126
7	5	261	270
7	9	133	124
7	11	68	30
6	10	148	140
6	9	88	82
6	8	251	249
6	7	128	128
6	6	85	65
6	5	144	143
6	4	84	87
6	3	89	90
6	2	250	247
6	1	53	66
6	0	87	92
6	-1	173	176
6	-2	253	248
6	-3	61	56
6	-4	57	69
6	-6	118	113
6	-7	100	71
6	-8	180	175
6	-9	97	112
6	-10	156	142
6	-11	114	103
6	-12	81	79
5	-12	91	90
5	-10	142	146
5	-9	191	193
5	-8	156	142
5	-7	153	143
5	-4	179	176
5	-2	48	53
5	-1	184	187
L	-		
5	1	440	410
5	2	306	288
5	3	305	294
5	4	208	201
5	5	97	88
5	6	202	202
5	7	237	240
5	8	174	172
5	9	193	193
5	11	83	66
5	13	134	116
4	13	142	129
4	12	210	208
4	11	98	97
4	9	70	46
4	3	159	153
4	2	394	383
4	1	180	179
4	0	165	149
4	-2	56	55
4	-3	172	163
4	-4	404	392
4	-5	167	163
4	-6	202	200
4	-7	163	152
4	-8	50	40
4	-9	64	55
3	-13	144	141
3	-12	129	107
3	-11	155	166
3	-10	130	122
3	-8	202	197
3	-7	182	179
3	-6	230	230
3	-5	430	414
3	-4	172	154
3	-3	50	67
3	-1	83	75
3	1	205	206
3	2	107	88
3	3	144	126
3	4	54	65
3	5	322	323
3	6	105	106
3	7	169	150
3	8	183	180
3	10	184	187
3	11	121	122
3	12	84	83
3	13	214	212
3	14	152	146
2	14	160	142
2	13	75	50
2	12	66	58
2	8	54	68
2	6	304	329
2	5	179	185
2	4	261	262
2	3	179	182
2	2	119	114
2	1	108	101
2	-1	102	96
2	-2	293	294
2	-3	157	156
2	-6	221	216
2	-7	69	71
2	-10	101	113
2	-11	114	100
2	-12	194	201
1	-14	69	28
1	-13	91	86
1	-12	80	64
1	-11	93	107
1	-10	123	101
1	-9	186	191
1	-8	119	125
1	-7	133	130
1	-6	136	116
1	-5	134	125
1	-4	285	282
1	-3	557	564
1	-2	254	252
1	2	175	186
1	3	45	55
1	4	147	140
1	5	143	150
1	6	111	97
1	8	97	94
1	10	204	209
1	10	54	42
1	11	58	30
1	14	83	99
0	14	64	63
0	13	87	33
0	10	161	156
0	9	160	157
0	8	281	298
0	7	173	183
0	6	55	43
0	5	167	176
0	4	317	317
0	3	120	121
0	2	319	346

eter shifts were less than 16 % of their corresponding standard deviations. The R-value was now 0.043.

The decrease in the R-value from 0.049 to 0.043 was shown, using the Pawley (1970)[15] simplification of the method proposed by Hamilton,[16] to be significant with a probability greater than 99 %. The R-ratio is 1.140 and should be compared with the calculated ratio $\mathcal{R}_{56,2777,\,0.01} = 1.015$. The indices 56, 2777 and 0.01 refer to the dimension of the hypothesis, the number of degrees of freedom, and the significance level, respectively.

A final difference Fourier map was calculated and no abnormalities could be detected in it. Lists of the final positional and thermal parameters are given in Tables 1a and 1b. The observed and calculated structure factors are given in Table 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The coordination around the copper atom is a distorted octahedron. One bond is formed to the oxygen [O(5)] of the water molecule, and *trans* to it is a bond to an oxygen [O(3)] of a sulphate group. The remaining four bonds are to nitrogens of the imidazole rings and to an oxygen [O(2)] in a second, symmetry-related sulphate group. Thus infinite chains are formed with the sulphate group bridging successive copper atoms (Fig. 2). The chains run in the b-direction along the two-fold screw axes. The symmetry-related chains are held together by hydrogen bonds and van der Waals forces.

Table 3. Bond lengths and bond angles, and their estimated standard deviations, for the atoms around copper.

Bond length (Å)		Angle (°)	
Cu–N1	1.999(3)	N1–Cu–N3	178.1(1)
Cu–N3	2.002(3)	N5–Cu–O2	176.7(1)
Cu–N5	1.995(3)	O3–Cu–O5	177.6(1)
Cu–O2	2.015(2)	N1–Cu–N5	89.9(1)
Cu–O3	2.578(2)	N5–Cu–N3	91.4(1)
Cu–O5	2.478(3)	N1–Cu–O2	88.2(1)
		N3–Cu–O2	90.6(1)
		O2–Cu–O3	88.1(1)
		O3–Cu–N5	89.2(1)
		O2–Cu–O5	93.0(1)
		N5–Cu–O5	89.9(1)
		O3–Cu–N1	90.2(1)
		O3–Cu–N3	91.2(1)
		O5–Cu–N1	92.0(1)
		O5–Cu–N3	86.7(1)

The coordination around copper. The copper atom is surrounded by three nitrogens and three oxygens. The arrangement is shown in Fig. 1 and distances and angles are given in Table 3. The mean of the three equatorial bond lengths for Cu–N is 1.999(3) Å, which is normal.[1-5] All the Cu–N bonds are within two standard deviations of this value. The fourth equatorial bond Cu–O(2) is 2.015(2) Å long. Of the three imidazole rings one ring is almost coplanar with the coordination plane around copper (counting the atoms N(1), N(3), N(5), O(2), and Cu), one is almost perpendicular to that plane and the third deviates about 45°. Apparently this does not produce any significant differences in the copper-nitrogen bond lengths. The apical bond

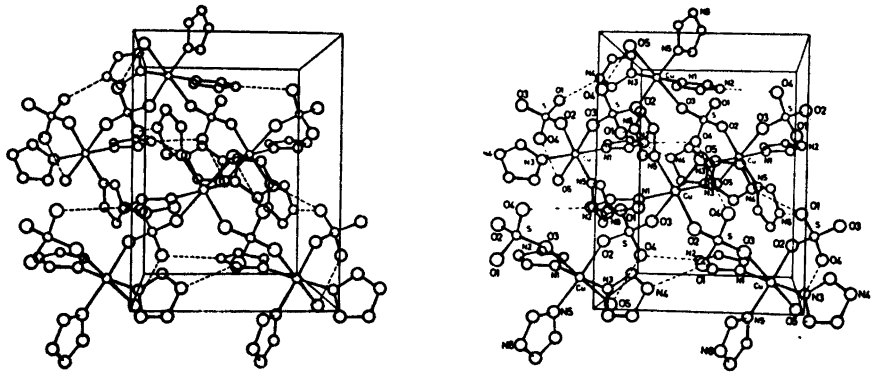

Fig. 2. A stereoscopic illustration of the molecular packing of $[Cu(H_2O)(C_3H_4N_2)_3SO_4]$, viewed along the a-axis. The parenthesis around the numbers are omitted in the figure.

length Cu – O(3) is 2.578(3) Å, which is in good agreement with a recent determination[3] [2.574(4) Å] for a bond between copper and a sulphate oxygen, but much longer than the average 2.41 Å in the same kind of bond in $CuSO_4.5H_2O$.[17] The other apical bond Cu – O(5) is 2.478(3) Å long, which is in good agreement with the range for a copper-water oxygen separation tabulated by Blount *et al.*,[18] but much longer than the 2.19 Å found in $(NH_4)_2Cu(SO_4)_2.6H_2O$,[19] where water oxygens are also in the apical positions in the coordination octahedron around copper. With these four short and two long bond distances the octahedron is seen to be distorted as expected.[20] The octahedron is also angularly distorted which is shown from significant differences for almost all of the angles compared to the ideal ones. The greatest difference is 3.3(1)° [O(5) – Cu – N(3)].

The sulphate group. In the sulphate group the oxygens are arranged in a tetrahedron which is nearly ideal, although three of the six tetrahedral angles differ significantly from the ideal one. The deviations are 1.7(2)° for [O(1) – S – O(2)]; 0.9(2)° for [O(1) – S – O(3)], and 1.0(2)° for [O(2) – S – O(3)]. The differences in sulphur-oxygen bond lengths do not seem to depend on whether the oxygen atoms are coordinated to a copper atom or not.

Bond distances and angles are given in Table 4. The sulphur-oxygen bond distances are in good agreement with those given in the recent tabulation by Andreetti, Cavalca and Musatti.[21]

Water and hydrogen bonds. The distances of the water hydrogens to the water oxygens are 0.96(6) Å for H(13) and 0.87(6) Å for H(14). This is longer than expected when a comparison is made with similar bonds in $MoO_3.2H_2O$,[22] where the range of distances in sixteen O – H bonds is 0.69(5) – 0.84(5) Å, considering that both determinations are from X-ray data. The O – H distances in $CuSO_4.5H_2O$ [17] calculated from neutron diffraction data have a mean value of 0.96 Å and our values should therefore show a reasonable shortening of at least 0.1 Å.[23]

Table 4. Bond lengths and bond angles, and their estimated standard deviations, for the sulphate group.

Bond lengths (Å)		Angle (°)	
S – O1	1.473(3)	O1 – S – O2	107.8(2)
S – O2	1.480(3)	O1 – S – O3	110.4(2)
S – O3	1.457(3)	O1 – S – O4	109.5(2)
S – O4	1.489(3)	O2 – S – O3	110.5(2)
		O2 – S – O4	109.3(2)
		O3 – S – O4	109.5(2)

It seems possible that the distances found in this determination depend on the oxygen coordination to copper and the two hydrogen bonds formed to sulphate oxygens. These hydrogen bond lengths are [O(4)···H(13) – O(5)] = 2.813(4) Å and [O(4)···H(14) – O(5)] = 2.776(4) Å and the deviation of the bonds is such that the angle H(13) – O(5) – H(14) is 97 (5)° which is smaller than those in $MoO_3 \cdot 2H_2O$ [mean value 109(6)°].

The hydrogen atoms on the imidazole nitrogens also take part in a hydrogen bonding scheme. The acceptor atoms are sulphate oxygens which are not copper-coordinated. Hydrogen bonds within the symmetry-related chains are [N(2) – H(4)···O(4)] = 2.847(4) Å, [N(4) – H(8)···O(1)] = 2.871(4) Å and [O(5) – H(14)··· O(4)] = 2.776(4) Å. Those between the chains are [N(6) – H(12)···O(1)] = 2.762(4) Å and [O(5) – H(13)···O(4)] = 2.813(4) Å. No significant difference of the hydrogen bond distances between N – O and O – O can be seen. All hydrogen bond lengths are of the same magnitude as those found in similar structures.[3,4]

The imidazole rings. Interatomic distances and angles for the imidazole rings are given in Table 5. Considering the standard deviations there are no significant differences in the bond distances and angles for the three rings. Bond distances and angles between carbons and nitrogens are also about the same as those found in other structure determinations.[1–5] The bond distance range for hydrogens to carbons and nitrogens is 0.81(5) Å to 0.96(5) Å. Planes through the positions of the nitrogen and carbon atoms in respective imidazole rings were calculated and have the equations

1. $0.2334\,x + 0.0764\,y - 0.9694\,z + 0.2486 = 0$ [N(1), N(2), C(1), C(2), C(3)]
2. $0.7265\,x - 0.4784\,y - 0.4933\,z + 1.7762 = 0$ [N(3), N(4), C(4), C(5), C(6)]
3. $-0.4940\,x - 0.8414\,y - 0.2192\,z - 3.4449 = 0$ [N(5), N(6), C(7), C(8), C(9)]

The maximum deviations of non-hydrogen atoms from the planes are 0.001 Å, 0.004 Å, and 0.003 Å for the first, second, and third imidazole

Table 5. Bond lengths and bond angles, and their estimated standard deviations, for the imidazole rings.

Bond length (Å)		Angle (°)	
N1–C1	1.313(5)	C3–N1–C1	105.9(3)
N1–C3	1.367(5)	N1–C1–N2	110.7(3)
N2–C1	1.337(5)	C1–N2–C2	107.8(3)
N2–C2	1.357(6)	N2–C2–C3	106.1(3)
C2–C3	1.347(6)	C2–C3–N1	109.5(3)
N3–C4	1.321(5)	C6–N3–C4	105.0(3)
N3–C6	1.381(5)	N3–C4–N4	111.5(3)
N4–C4	1.337(5)	C4–N4–C5	107.3(3)
N4–C5	1.369(5)	N4–C5–C6	106.3(4)
C5–C6	1.342(6)	C5–C6–N3	109.9(3)
N5–C7	1.319(5)	C9–N5–C7	106.7(3)
N5–C9	1.377(5)	N5–C7–N6	110.2(3)
N6–C7	1.340(5)	C7–N6–C8	108.2(3)
N6–C8	1.361(6)	N6–C8–C9	106.4(3)
C8–C9	1.358(6)	C8–C9–N5	108.6(3)
H1–C1	0.94(5)	H1–C1–N1	127.1(32)
H2–C2	0.92(6)	H1–C1–N2	122.2(32)
H3–C3	0.94(5)	H2–C2–N2	122.2(41)
H4–N2	0.81(5)	H2–C2–C3	131.5(40)
H5–C4	0.89(5)	H3–C3–N1	119.1(28)
H6–C5	0.95(5)	H3–C3–C2	131.2(28)
H7–C6	0.96(5)	H4–N2–C1	128.8(36)
H8–N4	0.90(5)	H4–N2–C2	123.4(36)
H9–C7	0.96(5)	H5–C4–N3	121.2(34)
H10–C8	0.95(5)	H5–C4–N4	126.7(34)
H11–C9	0.87(4)	H6–C5–N4	126.4(33)
H12–N6	0.92(5)	H6–C5–C6	127.2(34)
		H7–C6–C5	128.6(26)
		H7–C6–N3	121.4(26)
		H8–N4–C4	122.3(31)
		H8–N4–C5	130.1(31)
		H9–C7–N5	124.9(29)
		H9–C7–N6	124.4(29)
		H10–C8–N6	122.2(33)
		H10–C8–C9	131.4(33)
		H11–C9–C8	128.0(30)
		H11–C9–N5	123.2(29)
		H12–N6–C7	122.5(29)
		H12–N6–C8	129.2(29)

rings, respectively. The corresponding maximum deviations of hydrogens are 0.06 Å [H(3)], 0.12 Å [H(5)], and 0.11 Å [H(9)] Å, respectively. None of these hydrogen atoms is involved in hydrogen bonds.

Conclusions. This structure determination has shown that when the anion is sulphate and the ratio of imidazole to copper is 3:1 the coordination around copper in the equatorial plane is formed by three imidazole nitrogens and a sulphate oxygen. The water molecule can thus not compete with the oxygen of the anion. We think that the systematic change of anions and different ratios of imidazole to copper will show (as described in the introduction) differences in coordination of the anions to copper. This in turn will provide us with more variations in copper-imidazole interactions than has hitherto been found.

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