tical, the diameter being greater perpendicular to the *b* axis than parallel to **b**.

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The Crystal Structures of Copper Tetrammine Complexes A. $Cu(NH_3)_4SO_4 . H_2O$ and $Cu(NH_3)_4SeO_4$*

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The room temperature crystal structures of two copper tetrammine complexes have been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data. The space group for $Cu(NH_3)_4SO_4 . H_2O$ is *Pnam* with lattice constants $a_0 = 10{\cdot}651$, $b_0 = 11{\cdot}986$, and $c_0 = 7{\cdot}069$ Å; that for $Cu(NH_3)_4SeO_4$ is $P2_1/n$ with lattice constants $a_0 = 10{\cdot}313$, $b_0 = 10{\cdot}259$, $c_0 = 7{\cdot}405$ Å and $\beta = 104{\cdot}43°$. In both complexes, the copper ion is surrounded by four ammonia molecules ($\sim 2{\cdot}0$ Å) in a near square planar arrangement and by two more distant oxygen atoms (but at unequal distances from the copper ion). The copper ions are connected *via* the oxygen atoms in a chain-like arrangement, and a network of hydrogen bonds hold these chains and ions together.

Introduction

The magnetic and thermal properties of $Cu(NH_3)_4SO_4.H_2O$ (CTASUL) have been extensively studied and have been interpreted as those of a substance containing a magnetic linear chain structure (Saito & Kanda, 1967; Rogers, Carboni & Richards, 1967). Recently Saito & Kanda (1967) conducted proton nuclear magnetic resonance studies on this material in the paramagnetic and ordered state. Unfortunately the lack of proton positions prevented a quantitative interpretation of these data. Since the early crystallographic study by Mazzi (1955)) reported a structure based on projected data (with overlapping atomic sites) and indicated an unusual coordination about the copper ion, a detailed structure determination was considered necessary for any future quantitative interpretation of the observed resonance data.

Our attempts to crystallize an isostructural selenate compound proved to be unsuccessful; however, we isolated several other copper tetrammine complexes. The crystal structure of one of these complexes, $Cu(NH_3)_4SeO_4$ (CTASEL), was determined and the coordination about the copper was shown to be distorted in a similar manner to that found in CTASUL. The room temperature X-ray diffraction studies on these two compounds reported here are part of a program to gain an understanding of the relationship between chemical bonding and magnetic properties in materials containing linear chain structures.

Experimental

The deep blue crystals of both compounds were grown in the interface between an alcohol layer and an aqueous solution, prepared by adding an excess of NH_3 to the required copper salt solution. Crystals were examined by X-ray photographic techniques to insure that a single-crystal specimen rather than a twin was selected for our measurements. The space groups were selected on the basis of the observed extinctions on Mo $K\alpha$ precession photographs and the absence of a piezoelectric response. In addition, the statistics of the normal structure factors calculated from the intensity data on CTASEL corroborated a centrosymmetric space group. The final agreement between the observed and calculated structure factors indicate that the space groups selected are the correct choice. The cell edges have been selected to conform to Donnay's (1943) rules, and hence, may not agree with other published results. Specific values found from our experimental procedures are summarized in the following section.

The lattice constants for these complexes were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1{\cdot}54050$ Å) by least-squares fit of high 2θ values measured on films taken with a 115 mm diameter Weissenberg camera utilizing Straumanis film loading.

Three-dimensional Mo $K\alpha$ intensity data were measured using the θ–2θ scan technique on a Picker dif-

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fractometer equipped with a Datex automatic control module for setting the angles on the E&A full circle Eulerian orienter and with a scintillation counter employing pulse-height discrimination.

Intensity data were collected with both crystals mounted along their longest direction. A unique set of intensity data was obtained for each complex by averaging two symmetry related sets after absorption corrections, calculated from the shape of the specimen used, had been applied.

Lorentz and polarization factors were applied and structure factors calculated using Cu^{2+}, S, Se, O and H scattering factors from Table 3·3·1A (p. 202) and dispersion corrections for copper and selenium from Table 3·3·2C (p. 215) of *International Tables for* X-*ray Crystallography* (ITXC).

Crystal data

CTASUL: Space group, *Pnam* with $k+l$ odd for $0kl$'s and h odd for $h0l$'s absent; coordinates of equivalent positions, general eightfold (d) positions are $\pm(x,y,z)$, $\pm(x,y,\frac{1}{2}-z)$, $\pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$ and $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z)$ and fourfold mirror (c) positions are $\pm(x,y,\frac{1}{4})$ and $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{4})$; lattice constants, $a_0=10{\cdot}6509(7)$, $b_0=11{\cdot}9860(16)$, $c_0=7{\cdot}0690(3)$ Å determined from 88 2θ values; $Z=4$, $d_{\text{reported}}=1{\cdot}81$ g.cm^{-3}, $d_{\text{calc}}=1{\cdot}74$ g.cm^{-3}; intensities, 1012 observed and 396 unobserved; size of data crystal, $\sim 0{\cdot}14\times 0{\cdot}17\times 0{\cdot}34$ mm, bound by {110} and {001}, $\mu_{MoK\alpha}=27{\cdot}2$ cm^{-1}.

CTASEL: Space group, $P2_1/n$ with $h+l$ odd for $h0l$'s and k odd for $0k0$'s absent; coordinates of equivalent positions, general fourfold (e) positions are $\pm(x,y,z)$ and $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; lattice constants, $a_0=10{\cdot}3128$ (4), $b_0=10{\cdot}2590(3)$, $c_0=7{\cdot}4046(3)$ Å and $\beta=104{\cdot}431(3)°$ determined from 94 2θ values; $Z=4$, $d_{\text{observed}}=2{\cdot}43$ g.cm^{-3}, $d_{\text{calc}}=2{\cdot}41$ g.cm^{-3}; intensities, 1537 observed, 209 unobserved and 5 extinct; size of data crystal, $\sim 0{\cdot}15\times 0{\cdot}14\times 0{\cdot}38$ mm, bound by {100}, {110} and {001}, $\mu_{MoK\alpha}=84{\cdot}0$ cm^{-1}.

Structure determination

Initial positional parameters used for CTASUL were those determined by Mazzi (1955). In space group *Pnam*, Mazzi selected the copper atom, water molecule and sulfate ion to lie in fourfold (c) positions on the mirror planes at $y=\pm\frac{1}{4}$ and the ammonia molecules and a set of oxygen atoms of the sulfate ion in general eightfold (d) positions. Three cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters resulted in a reliability index, $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ equal to 0·081. The function, $\Sigma w(F_o-F_c)^2$, was minimized; weights were assigned from counting statistics; the unobserved reflections were assigned zero weight if $|F_0|>|F_c|$. A Fourier synthesis suggested the need for anisotropic thermal parameters; such parameters were used in the four cycles of subsequent refinement. Hydrogen positions (Table 1) obtained from a difference synthesis, were assigned an isotropic thermal parameter, B, equal to 4.0 Å^2 and were included as fixed atom contributions in the subsequent three cycles of least-squares refinement. The average and maximum parameter shifts as parts of the estimated standard deviation for the last cycle are 0·03 and 0·13, respectively; the final value of R is 0·047. Final atomic positional and anisotropic thermal parameters are given in Tables 2 and 3 and the list of observed and calculated structure factors appear in Table 4. The correctness of the structure was verified by final Fourier and difference syntheses.

Table 1. *Hydrogen atom positional coordinates for* $Cu(NH_3)_4SO_4.H_2O$

		x	y	z
H(1)	O(1)	0·270	0·120	0·350
H(2)	N(1)	0·120	0·305	0·570
H(3)		0·110	0·410	0·410
H(4)		0·010	0·370	0·540
H(5)	N(2)	0·400	0·310	0·560
H(6)		0·390	0·410	0·410
H(7)		0·510	0·375	0·520

Table 2. *Final atomic coordinates for* $Cu(NH_3)_4SO_4.H_2O$

Cu	−0·00748 (6)	0·25872 (5)	¼
S	0·25267 (10)	0·11405 (9)	¼
N(1)	0·07132 (31)	0·35355 (26)	0·04365 (49)
N(2)	0·43758 (32)	0·34695 (26)	0·04110 (52)
O(1)	0·29653 (61)	0·15310 (59)	¼
O(2)	0·19335 (32)	0·06807 (29)	0·58073 (43)
O(3)	0·24729 (58)	0·23530 (34)	¼
O(4)	0·38534 (42)	0·07966 (45)	¼

Table 3. *Anisotropic temperature factors* B_{ij} *for* $Cu(NH_3)_4SO_4.H_2O$

The temperature factor is of the form $\exp(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*)$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2·60 (2)	2·14 (2)	2·25 (2)	0·20 (2)	—	—
S	1·98 (3)	1·84 (3)	1·72 (3)	−0·00 (3)	—	—
N(1)	3·67 (13)	2·87 (12)	2·55 (13)	−0·34 (9)	0·22 (11)	0·18 (10)
N(2)	3·72 (13)	2·62 (11)	2·97 (14)	0·17 (9)	0·09 (12)	0·41 (11)
O(1)	7·24 (32)	8·74 (37)	2·40 (17)	−5·06 (29)	—	—
O(2)	5·00 (14)	4·90 (14)	2·47 (11)	−1·75 (12)	−0·54 (11)	−0·45 (11)
O(3)	7·47 (29)	2·24 (15)	4·06 (18)	1·18 (19)	—	—
O(4)	3·15 (17)	5·58 (24)	3·98 (20)	0·77 (16)	—	—

Table 4. *Observed and evaluated structure factors for* CTASUL

K	10FO	10FC
H= 0 L= 0		
2	1161	-1129
4	825	-270
6	832	-827
8	727	742
10	551	-553
12	260	262
14	164	-166
16	148	113
H= 1 L= 0		
1	144	-138
2	1047	-1018
3	216	222
4	612	-608
5	108	-108
6*	10	3
7	198	189
8	362	390
9	309	-292
10	124	-126
11	231	-230
12	77	-72
13	169	-163
14	67	60
15	105	129
16	128	127
H= 2 L= 0		
0	228	230
1	152	173
2	1131	-1128
3	93	+121
4	711	779
5	54	-72
6	54	-66
7	49	-65
8	403	355
9*	49	52
10	540	-530
11*	55	-26
12	351	352
13*	62	64
14*	56	-14
15*	62	-20
16*	32	12
H= 3 L= 0		
1	156	-152
2	1280	1270
3	125	-119
4	297	-316
5	141	-130
6	414	+428
7	411	422
8	161	164
9	206	-189
10	183	182
11	191	194
12*	62	-53
13	172	-182
14*	58	-17
15	95	118
16*	72	-62
H= 4 L= 0		
0	1250	1260
1	187	217
2	893	+961
3*	38	104
4	569	575
5	401	427
6	669	-659
7*	46	-42
8	736	682
9	71	-60
10	263	-236
11	135	-138
12	88	105
13*	62	46
14	276	-274
15*	45	-8
16	146	151
H= 5 L= 0		
1	301	300
2	121	132
3	249	258
4	109	-94
5	317	-315
6*	12	3
7*	48	-43
8	312	315
9	245	-239
10	235	-226
11	161	163
12	162	-158
13	92	-100
14*	69	64
15	152	152
H= 6 L= 0		
0*	36	-49
1	183	175
2	397	+380
3	354	-373
4	877	867
5	125	-145
6	514	-499
7	79	-101
8	65	67
9	178	189
10	233	-236
11*	61	-48
12	229	241
13	97	90
14*	70	-59
15*	71	-40

K	10FO	10FC
H= 7 L= 0		
1	82	-88
2	238	265
3*	47	-38
4*	35	11
5	130	-129
6	252	-233
7	272	262
8*	56	-70
9	95	-88
10	131	119
11	118	136
12	98	115
13	147	-146
14*	71	-59
H= 8 L= 0		
0	438	407
1	129	147
2	405	-367
3	179	-182
4	382	386
5	158	163
6	541	-539
7	72	-72
8	410	388
9	131	132
10*	69	11
11	86	-94
12*	60	47
13*	49	19
14	237	-236
H= 9 L= 0		
1	113	-123
2	241	-243
3	128	124
4	91	88
5*	55	-29
6	170	174
7	107	113
8	60	65
9	71	-91
10	163	-160
11*	63	61
12*	62	-23
13	111	-112
H= 10 L= 0		
0	145	134
1	225	219
2	210	-224
3*	55	-43
4	411	422
5	125	126
6	242	-221
7	137	-143
8*	16	7
9*	63	67
10	184	-190
11	93	-78
12	163	163
H= 11 L= 0		
1*	56	19
2*	57	-22
3	64	62
4	73	62
5	90	-100
6	110	-110
7*	53	27
8	108	-106
9	69	-67
10	74	74
11	107	100
H= 12 L= 0		
0	324	318
1	97	94
2	199	-203
3	153	-136
4*	54	37
5	106	105
6	174	-169
7	87	-92
8	252	235
9	82	64
10*	73	-37
H= 13 L= 0		
1*	65	-35
2	176	-164
3*	65	46
4*	36	7
5*	65	-23
6	105	103
7*	64	37
8*	71	60
H= 14 L= 0		
0*	63	46
1	84	89
2	156	-149
3	77	-70
4	170	167
5	101	93
H= 0 L= 1		
1	650	-584
3	1412	1420
5	248	-205
7	153	93
9	525	-506
11	476	463
13	184	-171
15*	4	1
H= 1 L= 1		
1	772	751

K	10FO	10FC
2	116	87
3	122	-123
4	260	-271
5	438	-449
6	222	206
7	179	-158
8	205	-190
9	259	262
10	247	246
11*	56	-46
12	200	-208
13	87	-87
14	150	154
15*	67	-40
16	128	-129
H= 2 L= 1		
0	146	120
1	1557	-1563
2	131	-159
3	602	568
4	59	74
5	851	-799
6*	43	28
7	918	921
8	47	47
9	516	-509
10*	54	-71
11	154	164
12*	52	20
13	207	-210
14*	51	-11
15	234	238
16*	41	10
H= 3 L= 1		
1	100	-109
2	85	-90
3	16	-3
4	145	-134
5	148	185
6	203	193
7	99	82
8	252	-255
9	348	-343
10	221	213
11	75	68
12	157	-143
13	147	132
14	138	146
15*	69	66
16	109	-128
H= 4 L= 1		
0	209	-226
1	513	-481
2	202	-222
3	781	751
4	239	237
5	643	-657
6	54	-59
7	159	153
8	135	137
9	233	-220
10*	55	-31
11	438	431
12*	58	37
13	155	-165
14*	68	-67
15*	9	3
16*	62	26
H= 5 L= 1		
1	217	247
2	335	355
3	239	-273
4*	27	-5
5	222	-234
6	219	226
7	163	175
8	202	-195
9	209	215
10	108	112
11*	61	-52
12	201	-200
13	121	-123
14	147	150
15*	61	-22
H= 6 L= 1		
0	447	465
1	773	-814
2	102	-97
3	413	377
4	78	87
5	468	-440
6	158	-160
7	686	679
8*	38	17
9	342	-343
10	131	-123
11*	52	43
12	95	91
13	179	-175
14*	54	-10
15	197	204
H= 7 L= 1		
1	268	-262
2*	46	-26
3	183	196
4	115	-107
5	211	211
6	93	75
7*	50	-18
8	177	-172
9	251	-242
10	173	167
11*	63	57

K	10FO	10FC
12	97	-87
13*	69	63
14	96	103
H= 8 L= 1		
0	202	203
1	133	-137
2	131	-130
3	577	597
4	95	89
5	482	-475
6	190	-183
7	77	74
8	143	146
9	133	-139
10*	63	-54
11	256	260
12*	66	61
13	115	-104
14	85	-56
H= 9 L= 1		
1	55	130
2*	53	-31
3	106	-104
4	163	-162
5	162	-177
6	117	136
7	88	87
8*	61	-50
9	122	125
10	97	102
11*	51	17
12	112	-114
13	131	-115
H= 10 L= 1		
0	72	72
1	405	-400
2	186	-188
3	202	186
4	176	178
5	155	-146
6*	60	-54
7	336	336
8	88	88
9	205	-204
10	84	-94
11*	36	13
12*	69	59
H= 11 L= 1		
1	94	-100
2	84	81
3	150	147
4*	59	-20
5	70	72
6*	58	35
7*	67	-65
8	79	-82
9	138	-133
10	94	86
11*	71	51
H= 12 L= 1		
0	142	138
1	90	-102
2	107	-107
3	245	249
4	79	82
5	225	-221
6	108	-103
7*	50	25
8	87	104
9	72	-79
H= 13 L= 1		
1	91	77
2*	33	7
3*	68	-49
4*	67	-34
5	123	-109
6*	69	66
7*	68	42
8*	73	-51
H= 14 L= 1		
0	70	64
1	211	-201
2	97	-86
3*	38	14
4	111	107
H= 0 L= 2		
0	1163	-1180
2	946	959
4	906	-820
6	1094	1070
8	738	-727
10	85	72
12	138	-122
14	349	350
16	183	-191
H= 1 L= 2		
1	327	323
2	940	879
3	204	-183
4	308	-255
5	118	96
6	390	-392
7	294	-285
8	85	-71
9	171	159
10	215	234
11	164	-158
12*	56	36
13	196	199
14*	20	-3

K	10FO	10FC
15	156	-155
16	105	-102
H= 2 L= 2		
0	237	181
1	337	-354
2	406	391
3	294	-312
4	1300	-1227
5	100	-126
6	727	687
7	110	117
8	74	-52
9*	50	-5
10	314	302
11*	58	60
12	293	-301
13*	12	-1
14	67	79
15*	40	10
16	83	-93
H= 3 L= 2		
1	251	-286
2	238	156
3	103	-91
4	60	-47
5	341	340
6	130	114
7	136	-128
8	273	287
9	223	222
10	215	-212
11	190	-192
12	218	-208
13	138	153
14	97	99
15	144	-151
16	128	125
H= 4 L= 2		
0	1089	-1150
1*	40	39
2	939	928
3	260	271
4	450	-395
5	141	-131
6	554	533
7	129	131
8	670	-671
9	83	-77
10	214	218
11*	1	-0
12	126	-124
13*	63	-25
14	244	248
15*	61	25
H= 5 L= 2		
1	166	157
2	568	613
3	204	-198
4	176	-178
5	116	113
6	296	-287
7	100	-93
8*	51	-32
9	137	134
10	183	185
11	190	-189
12*	56	-15
13	128	138
14*	64	23
15	97	-98
H= 6 L= 2		
0	350	-338
1	198	-192
2	599	598
3	110	116
4	546	-518
5	95	-101
6	105	76
7	117	108
8	184	-194
9	94	-114
10	414	428
11*	61	57
12	230	-243
13*	67	-37
14*	29	-10
15*	72	60
H= 7 L= 2		
1*	48	-34
2	303	-296
3	49	-30
4	191	-195
5	98	109
6	147	137
7	144	-147
8	145	158
9	174	173
10*	61	-46
11	140	-143
12	118	-114
13	111	117
14*	70	60
H= 8 L= 2		
0	905	-932
1	68	-60
2	376	371
3	221	230
4	54	-50
5	171	-166
6	375	373
7	124	114
8	365	-363

K	10FO	10FC
9	80	-76
10	184	173
11*	62	50
12	103	-104
13*	71	-51
H= 9 L= 2		
1	73	66
2	157	147
3	60	-53
4	123	124
5*	51	31
6	56	-39
7	109	-118
8	191	-190
9	116	109
10	109	111
11	82	-91
12*	72	56
13*	70	66
H= 10 L= 2		
0	136	-151
1	169	-159
2	297	299
3	105	100
4	313	-315
5	120	-130
6	83	92
7	94	97
8*	65	-82
9	77	-64
10	213	216
11*	69	64
12	159	-157
H= 11 L= 2		
1*	41	-9
2	191	-188
3*	41	-6
4*	35	-5
5*	62	57
6	167	161
7	99	-96
8*	64	-22
9	93	78
10*	72	-55
H= 12 L= 2		
0	272	-269
1	119	-120
2	159	155
3	79	93
4	91	-78
5	119	-111
6	204	199
7*	67	69
8	200	-197
9*	73	-55
H= 13 L= 2		
1*	53	-15
2	73	78
3*	66	-27
4	70	39
5	68	45
6*	70	-44
7*	71	-34
H= 14 L= 2		
0*	77	32
1	101	-99
2	108	115
3	83	80
4	225	-209
H= 0 L= 3		
1	247	217
3	845	-769
5	982	949
7	135	-132
9	177	147
11	389	-384
13	140	160
15	73	-71
H= 1 L= 3		
1	150	169
2	53	83
3	63	28
4	347	360
5	149	178
6	162	-154
7*	20	1
8	150	126
9	384	-375
10	224	-219
11*	36	-6
12	150	157
13	156	159
14	154	-155
15*	71	64
16	137	130
H= 2 L= 3		
0	145	207
1	704	696
2	288	305
3	879	-839
4	86	-73
5	658	647
6	148	-168
7	860	-847
8	157	-172
9	388	376
10*	56	45
11*	2	-0
12*	63	24
13	233	240

K	10FO	10FC
14*	60	24
15	247	-258
H= 3 L= 3		
1	199	198
2	250	-263
3	465	-476
4	122	-156
5	181	-138
6	248	-258
7	250	267
8	247	244
9	274	255
10	100	-91
11	121	-122
12	180	181
13*	64	-42
14	129	-134
15*	72	-63
H= 4 L= 3		
0	223	-251
1	474	439
2	56	-72
3	571	+605
4	109	-117
5	580	560
6	243	251
7	113	+84
8*	41	-5
9	226	227
10*	58	60
11	399	+401
12*	63	-34
13	115	127
14*	52	18
15*	38	-3
H= 5 L= 3		
1	72	-98
2	101	-92
3*	47	-21
4	264	268
5	273	255
6	77	-56
7	71	58
8	104	118
9	264	-252
10	171	-182
11*	83	-45
12	135	141
13	159	158
14	136	-140
15*	66	21
H= 6 L= 3		
0	90	-112
1	909	924
2	197	205
3	106	-109
4	116	-106
5	272	251
6	58	67
7	579	-559
8	106	-114
9	329	336
10*	58	49
11	130	-130
12*	67	-59
13	126	128
14*	65	34
H= 7 L= 3		
1	366	376
2	84	-74
3	184	-170
4*	18	-5
5	248	-261
6	99	-106
7*	58	-46
8	149	137
9	161	170
10	148	-143
11*	66	-47
12	104	112
13*	63	-24
14	73	-63
H= 8 L= 3		
0	148	-162
1	200	205
2	70	70
3	580	-578
4	123	-131
5	179	188
6	186	182
7*	56	-40
8	96	-89
9	247	244
10*	63	54
11	230	-245
12*	69	-37
13	94	84
H= 9 L= 3		
1	272	-264
2*	57	22
3	142	141
4	105	109
5	207	200
6	109	-102
7*	63	-74
8	74	90
9*	65	-44
10	86	-86
11*	58	11
12	81	90

Table 4 (*cont.*)

K	10FO	10FC
H= 10 L= 3		
0	91	-82
1	428	414
2	132	141
3	81	-77
4	148	-152
5	138	137
6	88	88
7	264	-273
8*	66	-47
9	192	189
10*	68	64
11*	73	-51
H= 11 L= 3		
1	67	75
2*	47	-8
3*	61	-31
4*	61	38
5	72	-70
6*	66	-37
7*	67	-31
8	68	73
9	126	122
10	110	-100
H= 12 L= 3		
0	71	-91
1	65	62
2	133	121
3	237	-241
4	85	-78
5	193	200
6*	64	54
7*	71	-43
8	132	-109
H= 13 L= 3		
1	104	-92
2*	47	-10
3	82	70
4*	8	-2
5	93	92
6*	74	-83
H= 14 L= 3		
0	95	-91
1	142	141
2	75	69
3*	72	-33
H= 0 L= 4		
0	1469	1452
2	894	-818
4	146	128
6	484	-480
8	646	639
10	253	-255
12	155	156
14	204	-205
H= 1 L= 4		
1	170	-179
2	368	-359
3	112	99
4*	62	6
5	69	-50
6	219	220
7	209	203
8	192	181
9	171	-170
10	171	-181
11	157	162
12	96	-93
13	150	-143
14*	65	33
15	105	99
H= 2 L= 4		
0	350	309
1	193	201
2	498	-474
3	130	133
4	688	674
5	95	89
6	328	-291
7	53	-42
8	133	111
9*	23	-5
10	392	-390
11*	63	-61
12	259	278
13*	60	24
14*	63	-13
15*	51	-11
H= 3 L= 4		
1	161	166
2	394	414
3	44	41
4	177	-160
5	211	-208
6	284	-285
7	149	131
8*	0	-0
9	199	-200
10	151	148
11	150	150
12*	62	51
13	119	-117
14*	64	-22
15	95	115
H= 4 L= 4		
0	786	819
1*	33	14
2	607	-613
3	195	-195
4	313	296
5	97	92
6	487	-464
7*	55	-66
8	536	514
9*	54	33
10	151	-153
11*	63	-34
12	91	92
13*	67	54
14	212	-208
H= 5 L= 4		
1	75	-75
2	149	-162
3	127	114
4	67	-65
5	128	-115
6	70	92
7	104	95
8	194	197
9	116	-107
10	148	-150
11	127	141
12*	68	-83
13	88	-104
14*	69	34
H= 6 L= 4		
0	10	-6
1	175	172
2	395	-393
3	117	-105
4	592	596
5*	51	46
6	238	-226
7*	57	-55
8	106	120
9	93	104
10	219	-232
11*	67	-66
12	158	175
13*	67	43
H= 7 L= 4		
1*	52	18
2	265	275
3*	49	25
4	128	121
5	97	-102
6	150	-139
7	133	138
8	91	-86
9	111	-112
10*	65	47
11	93	92
12	82	75
13	115	-110
H= 8 L= 4		
0	523	509
1	79	88
2	237	-232
3	139	-153
4	174	188
5	117	112
6	411	-416
7	91	-85
8	264	264
9	82	75
10*	66	-44
11	71	-62
12*	66	50
H= 9 L= 4		
1	71	-64
2	216	-209
3	66	70
4*	60	-37
5*	62	-47
6	76	79
7	78	75
8	90	85
9*	68	-74
10	109	-94
11*	69	67
H= 10 L= 4		
0*	55	55
1	130	136
2	216	-221
3	70	-77
4	301	310
5	78	85
6	117	-124
7	93	-95
8*	61	46
9	69	70
10	148	-143
H= 11 L= 4		
1*	48	-10
2*	63	53
3*	59	26
4*	66	60
5*	68	-53
6	104	-88
7*	68	62
8*	71	-51
9*	73	-45
H= 12 L= 4		
0	250	248
1	82	89
2	134	-139
3	72	-77
4*	61	42
5	96	101
6	148	-142
7*	74	-65
H= 13 L= 4		
1*	7	-1
2	108	-110
3*	67	37
4*	10	-2
H= 0 L= 5		
1	493	-489
3	711	684
5	100	-81
7*	37	32
9	400	-402
11	372	379
13	119	-95
H= 1 L= 5		
1	381	371
2	61	67
3	171	-164
4	130	-114
5	282	-267
6	119	108
7*	13	-2
8	136	-134
9	145	145
10	159	168
11*	64	-37
12	135	-141
13*	68	-47
14	93	96
H= 2 L= 5		
0	73	62
1	855	-859
2	74	-63
3	234	211
4	60	46
5	326	-305
6*	49	-12
7	543	536
8*	37	9
9	361	-360
10*	62	-34
11	120	136
12*	63	31
13	120	-128
14*	54	-13
H= 3 L= 5		
1*	46	-24
2*	51	-40
3	107	-114
4	96	-84
5	151	157
6	116	119
7	151	148
8	158	-154
9	272	-263
10	151	152
11*	40	-9
12	87	-95
13	157	143
14	92	91
H= 4 L= 5		
0	58	-72
1	251	-245
2	117	-120
3	542	520
4	122	135
5	425	-420
6	55	-27
7	84	103
8	88	70
9	143	-154
10*	62	-26
11	280	283
12*	63	33
13	107	-116
H= 5 L= 5		
1	236	242
2	123	142
3	258	-256
4*	49	-12
5	175	-171
6	136	148
7	185	183
8	139	-136
9	100	98
10	64	65
11	73	-63
12	126	-126
13*	72	-55
H= 6 L= 5		
0	233	246
1	392	-402
2	69	-73
3	235	234
4	66	57
5	350	-346
6	78	-89
7	449	446
8*	27	8
9	175	-178
10	85	-88
11*	35	-13
12	89	75
H= 7 L= 5		
1	148	-145
2*	51	-18
3	109	103
4*	60	-77
5	133	130
6	65	60
7*	39	-8
8	106	-109
9	174	-164
10	116	108
11*	66	36
12*	72	-53
H= 8 L= 5		
0	141	136
1*	51	-33
2	101	-100
3	392	407
4*	57	47
5	390	-386
6	91	-94
7	69	70
8	106	109
9*	66	-45
10*	70	-45
11	147	156
H= 9 L= 5		
1	65	59
2*	10	-2
3*	60	-28
4	106	-96
5	108	-119
6	84	96
7*	62	34
8*	67	-28
9	114	106
10*	68	55
H= 10 L= 5		
0	64	68
1	237	-243
2	108	-115
3	121	124
4	107	109
5	110	-116
6*	68	-39
7	237	235
8*	64	60
9	131	-128
H= 11 L= 5		
1	105	-101
2*	68	66
3	143	144
4*	66	-26
5*	69	56
6*	42	13
7	85	-82
H= 12 L= 5		
0	100	96
1	81	-78
2*	71	-70
3	160	170
4*	67	51
5	142	-143
H= 0 L= 6		
0	1013	-962
2	346	329
4	132	-130
6	500	497
8	337	-354
10	155	155
12	91	-91
H= 1 L= 6		
1*	52	32
2	407	395
3	101	-96
4	132	132
5	79	90
6	98	-104
7	96	-91
8	108	-114
9	114	124
10	67	74
11	116	-110
12*	63	30
13	93	100
H= 2 L= 6		
0*	20	8
1	55	-46
2	423	407
3	60	48
4	536	-528
5*	57	16
6	183	180
7*	59	45
8	143	-142
9*	64	-39
10	228	229
11*	1	-0
12	180	-185
13*	64	-20
H= 3 L= 6		
1*	55	57
2	261	-250
3*	17	1
4*	56	-43
5	75	74
6	128	140
7	174	-178
8*	62	56
9	77	85
10	106	-104
11	97	-101
12*	70	-49
13	108	110
H= 4 L= 6		
0	551	-572
1	63	-67
2	366	370
3*	35	-10
4	196	-189
5	165	-167
6	310	320
7*	59	43
8	350	-348
9*	58	9
10	112	118
11*	68	57
12*	72	-57
H= 5 L= 6		
1	63	-63
2	144	156
3	121	-108
4*	56	-18
5	120	115
6	96	-98
7*	35	-3
8	72	-74
9	124	129
10	129	116
11	93	-97
12*	72	48
H= 6 L= 6		
0	120	-124
1	82	-80
2	246	258
3	140	137
4	373	-375
5*	68	21
6	174	173
7*	64	75
8*	65	-48
9	74	-89
10	188	198
11*	46	14
H= 7 L= 6		
1*	59	28
2	108	-114
3*	60	12
4*	60	-26
5	62	61
6	135	125
7	125	-123
8	81	53
9*	67	61
10	85	-71
H= 8 L= 6		
0	320	-332
1	72	-66
2	219	227
3	97	57
4	89	-101
5	100	-57
6	203	212
7*	63	42
8	234	-238
9*	72	-63
H= 9 L= 6		
1*	65	49
2	85	97
3*	67	-52
4*	45	-10
5*	41	13
6	90	-87
7*	71	-63
8	73	-72
H= 10 L= 6		
0	89	-91
1	109	-112
2	132	143
3*	60	35
4	209	-220
5	77	-70
6	94	93
7	74	75
H= 11 L= 6		
1*	59	-18
2*	71	-59
3*	65	-20
4*	51	-11
5*	71	55
H= 0 L= 7		
1	67	55
3	525	-512
5	365	367
7	103	-101
9	84	100
11	154	-160
H= 1 L= 7		
1	148	-127
2*	58	-30
3*	30	-6
4	100	82
5	165	157
6	97	-99
7	66	56
8	76	79
9	159	-144
10	88	-83
11*	17	-3
H= 2 L= 7		
0	64	-53
1	359	355
2*	56	33
3	197	-199
4*	55	-14
5	335	339
6*	32	7
7	391	-388
8*	64	-29
9	156	154
10*	66	35
11*	57	-6
H= 3 L= 7		
1	177	184
2*	49	-9
3	192	-191
4*	60	65
5	112	-109
6	68	-70
7	110	108
8	96	98
9	79	92
10	92	-88
11*	74	-68
H= 4 L= 7		
0*	51	4
1	171	165
2*	60	60
3	332	-339
4	67	-52
5	254	266
6*	62	47
7*	64	-53
8	70	-70
9	103	117
10*	38	10
11	216	-219
H= 5 L= 7		
1*	60	-34
2	88	-90
3*	47	-11
4*	59	39
5	127	119
6	83	-76
7*	57	11
8*	66	61
9	158	-145
10	74	-68
H= 6 L= 7		
0	115	-103
1	388	403
2	62	49
3	88	-55
4	74	-61
5*	59	65
6	68	62
7	277	-271
8*	67	-26
9	198	203
H= 7 L= 7		
1	129	117
2*	63	-24
3	107	-106
4*	60	32
5	101	-102
6*	66	-25
7*	69	35
8	86	81
9	121	114
H= 8 L= 7		
0	77	-71
1	128	142
2	64	50
3	226	-237
4*	69	-55
5	118	137
6	102	93
7*	50	-4
H= 9 L= 7		
1	104	-98
2*	62	17
3	111	98
4*	70	56
5	101	95
6*	73	-56
H= 10 L= 7		
0*	68	-23
1	222	215
2	81	81
3*	73	-51
4	59	-90
H= 0 L= 8		
0	373	365
2	261	-254
4	130	145
6	264	-264
8	255	256
10*	72	-42
H= 1 L= 8		
1*	64	-41
2	196	-179
3*	61	37
4*	64	24
5*	66	-40
6	141	134
7	89	88
8*	65	35
9*	72	-72
H= 2 L= 8		
0*	53	48
1	79	69
2	190	-193
3*	66	35
4	370	363
5*	55	19
6	187	-184
7*	66	-28
8*	44	23
9*	33	8
H= 3 L= 8		
1*	65	42
2	80	68
3*	56	24
4*	52	16
5	100	-89
6	83	-84
7*	65	52
8	78	-72
9	85	-76
H= 4 L= 8		
0	332	355
1*	39	11
2	222	-233
3	83	-77
4	82	84
5*	61	31
6	187	-193
7*	68	-27
8	248	240
H= 5 L= 8		
1	71	-54
2	157	-162
3*	67	60
4*	45	9
5*	67	-29
6	115	106
7*	66	46
8*	69	42
H= 6 L= 8		
0*	65	80
1	79	73
2	188	-194
3*	66	-26
4	227	228
5*	66	42
6*	71	-59
7*	72	-41
H= 7 L= 8		
1*	55	13
2	116	114
3*	57	20
4*	71	54
5*	72	-49
6	82	-77
H= 8 L= 8		
0	300	294
1*	56	24
2	115	-122
3	85	-81
4*	44	19
H= 0 L= 9		
1	173	-179
3	199	206
5	156	-154
7*	24	9
H= 1 L= 9		
1*	67	54
2*	23	5
3	93	-77
4*	71	-59
5	82	-75
6*	64	37
7*	73	53
H= 2 L= 9		
0*	59	-20
1	255	-269
2*	70	-48
3	120	119
4*	61	23
5	79	-76
6*	67	22
H= 3 L= 9		
1*	62	-21
2*	68	42
3*	47	13
4*	66	15
5*	72	75
6*	71	63
H= 4 L= 9		
0*	69	58
1	85	-93
2*	17	-2
3	204	218
4*	66	33
5	168	-180
H= 5 L= 9		
1	103	101
2*	12	3
3	81	-87
4*	74	-65
H= 6 L= 9		
0*	63	30
1	187	-189
2*	74	-61

The initial model selected for CTASEL refined to a false minimum; and hence the sequential procedure is given in greater detail than would otherwise be necessary. A three-dimensional Patterson function was originally interpreted as sets of copper atoms at coordinates (0·475,0·30,0·72) and the selenium atoms at coordinates (0·485,0·21,0·21). Such an arrangement consists of copper and selenium atoms stacked nearly one upon another along the *b* axis and would distribute the ionic charge in an alternating and regular manner. At this time it was recognized that an alternative selection of the origin is also possible which would yield an arrangement in which copper atoms are stacked nearly upon one another along the *b* axis (selenium atoms also would stack upon one another); however, such an arrangement has the disadvantage of stacking similar charges upon one another. The original Cu and Se coordinates ($R=0·29$) provided the phases for a three-dimensional Fourier synthesis which, together with the chemical knowledge that the SeO_4^{2-} ion is tetrahedral and the $Cu(NH_3)_4^{2+}$ ion probably near-square planar, clearly indicated probable positions for the oxygen and nitrogen atoms. These oxygen and nitrogen positions were very reasonable considering chemical intuition. Hence these positional parameters were immediately subjected to full-matrix least-squares refinement. An *R* factor of 0·18 was obtained at the end of five cycles with parameter shifts at fractional parts of the estimated standard deviation. The difference sythesis calculated at this point contained peaks very near the copper and selenium atoms which were interpreted as implying that an incorrect model had been selected for refinement rather than that a false minimum had been reached by the least-squares procedure. Most puzzling were the reasonable packing of chains and near-neighbor separations of this structural arrangement. At this point alternative arrangements for the copper and selenium atoms (different origin for the original Patterson vectors and space group $P2/n$) were investigated. These also yielded *R* values between 0·30 and 0·40 for the copper and selenium atoms; however, the oxygen and nitrogen positions were not very readily obtained from the corresponding Fourier syntheses as had been the case for the original set of copper and selenium coordinates. The best *R* value for any of these models, with oxygen and nitrogen atoms included, was 0·22. This suggested a careful check of the intensity data as well as the original set of coordinates for the copper and selenium atoms was necessary. A careful re-evaluation of the original Patterson function suggested that the *x* coordinates originally used for the copper and selenium atoms should be interchanged. The resulting Fourier synthesis was very similar to the original one as might be expected; however, least-squares refinement of the slightly different atomic coordinates proceeded as desired to $R=0·049$. A three-dimensional difference synthesis provided the hydrogen positions listed in Table 5. An isotropic thermal parameter equal to 4·0 Å^2 was assigned to the hydrogen atoms, and they were included as fixed atom contributions in the subsequent three cycles of least-squares refinement. Five intensity data (002,020,022,200, and $20\bar{2}$) were considered to suffer from extinction and were not included in the calculation of *R*. The average and maximum parameter shifts as parts of the estimated standard deviations for the last cycle are 0·01 and 0·04, respectively; the final value of *R* is 0·047. Tables 6 and 7 list the final atomic positional and anisotropic thermal parameters, respectively. The observed and calculated structure factors appear in Table 8. Again, the correctness of the structure was verified by final Fourier and difference synthesis.

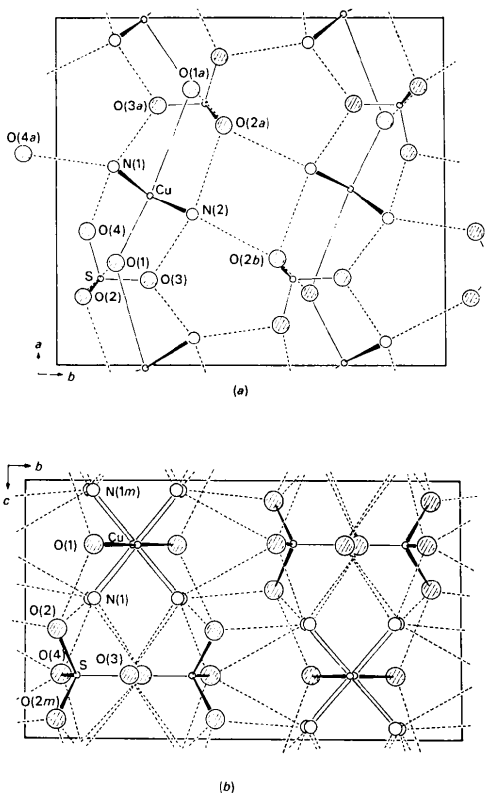

Fig. 1. (*a*) A representation of the crystal structure of $Cu(NH_3)_4SO_4.H_2O$ viewed along the *c* axis. Weak chains, which lie on the mirrors at $\frac{1}{4}$ and $\frac{3}{4}$ along **c**, are parallel to the **b** direction in this structure. Symmetry related atoms are labelled by an additional letter so that values listed in Table 9 can readily be found. Hydrogen bonding is indicated by dashed lines. (*b*). A representation viewed along the *a* axis.

In summary, one notes that the initial coordinates which were selected are quite close to the sets at (0·48, 0·30,0·71) and (0·48,0·20,0·21) which, with the similar scattering ability of the copper and selenium atoms, would by themselves define a subcell one-half the original unit cell. Hence, even though the structure is greatly overdetermined in this case with 10 atoms and over 1500 intensity data, care should have been employed with the procedure for initiating least-squares

Table 5. *Hydrogen atom positional coordinates for* $Cu(NH_3)_4SeO_4$

		x	*y*	*z*
H(1)	N(1)	0·630	0·500	0·750
H(2)		0·680	0·400	0·770
H(3)		0·620	0·440	0·650
H(4)	N(2)	0·390	0·520	0·800
H(5)		0·320	0·460	0·590
H(6)		0·280	0·410	0·760
H(7)	N(3)	0·630	0·150	0·585
H(8)		0·710	0·210	0·830
H(9)		0·590	0·085	0·760
H(10)	N(4)	0·333	0·165	0·820
H(11)		0·250	0·200	0·640
H(12)		0·370	0·085	0·660

Table 6. *Final atomic coordinates for* $Cu(NH_3)_4SeO_4$

	x	*y*	*z*
Cu	0·48774 (7)	0·30054 (7)	0·72191 (11)
Se	0·47518 (5)	0·21215 (5)	0·21171 (7)
N(1)	0·63535 (45)	0·43345 (44)	0·74824 (76)
N(2)	0·35941 (52)	0·44757 (52)	0·72585 (84)
N(3)	0·62190 (48)	0·16031 (47)	0·72558 (76)
N(4)	0·34136 (51)	0·16869 (53)	0·69558 (82)
O(1)	0·43087 (46)	0·31281 (44)	0·35891 (63)
O(2)	0·53275 (48)	0·29665 (56)	0·06289 (65)
O(3)	0·34399 (47)	0·12812 (55)	0·10225 (72)
O(4)	0·59094 (58)	0·11344 (53)	0·32485 (75)

refinement. More careful use of Fourier methods along with least-squares refinement may have prevented the incorrect solution obtained at the false minimum. In retrospect it was found that subjecting only the copper and selenium positions to least-squares refinement prior to calculating the difference or Fourier synthesis resulted in the correct nitrogen and oxygen positions needed for the final structure. Hence, extreme caution should be taken when atoms of nearly equal weight are nearly pseudosymmetrically related to one another.

Discussion

The most significant difference between the previous two-dimensional (Mazzi, 1955) and the present refinement on CTASUL is the location of the water molecule. This difference corresponds to a displacement of 0·2 Å; however, not in the direction which would make the two copper-oxygen separations more nearly equal. The present values of 2.339 and 3·475 Å [Table 9(*a*)] may be compared with 2·59 and 3.37 Å obtained with the projected data. These two copper–oxygen separations together with the more regular copper–nitrogen separations (2·031 Å) form a greatly distorted octahedral arrangement around the copper ion. When only the closer five neighbors are considered, the coordination consists of a slightly distorted [4+1] tetragonal pyramid in which the base of the pyramid is formed by the ammonia nitrogen atoms. The copper ion is slightly inside of this pyramid at a distance of 0·194 Å from the plane formed by the base (nitrogen atoms). Such an environment about a copper ion has previously been reported in $Cu(NO_3)_2 \cdot CH_3NO_2$ by Duffin & Wallwork (1966). In that complex the coordination about the copper ion consists of four oxygen atoms at ~1·95 Å which form the base of the pyramid

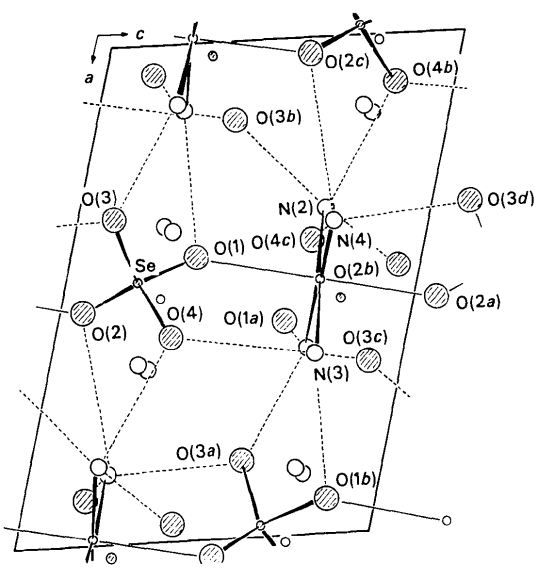

Fig. 2. A representation of the crystal structure of $Cu(NH_3)_4SeO_4$ viewed along the *b* axis. Solid lines indicating chemical bonding and dashed lines indicating hydrogen bonding are included only for atoms situated in the upper half of the unit cell. Labelling of symmetry related atoms with an additional letter should aid interpretation of Table 10. In this structure, the selenate ions are part of the chemical chain which connects the copper ions.

Table 7. *Anisotropic temperature factors* B_{ij} *for* $Cu(NH_3)_4SeO_4$

The temperature factor is of the form $\exp(-\frac{1}{4}\Sigma\ \Sigma\ B_{ij}h_ih_ja_i^*a_j^*)$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1·40 (2)	1·41 (3)	3·05 (3)	0·05 (2)	0·88 (2)	0·03 (2)
Se	1·41 (3)	1·38 (2)	1·85 (2)	−0·01 (1)	0·74 (1)	−0·02 (2)
N(1)	1·45 (16)	1·05 (15)	3·28 (21)	−0·10 (12)	1·15 (15)	0·09 (14)
N(2)	2·03 (20)	1·90 (19)	3·51 (24)	0·56 (15)	0·91 (17)	−0·28 (17)
N(3)	1·68 (17)	1·50 (17)	2·94 (20)	0·28 (14)	0·73 (15)	0·03 (15)
N(4)	1·81 (18)	1·94 (18)	3·35 (23)	−0·43 (15)	0·71 (16)	0·09 (17)
O(1)	2·88 (18)	2·03 (16)	2·45 (17)	0·81 (14)	1·04 (14)	−0·21 (13)
O(2)	2·65 (19)	4·17 (24)	2·35 (17)	−1·50 (17)	1·03 (14)	0·26 (17)
O(3)	2·32 (18)	3·70 (22)	3·13 (20)	−1·49 (17)	0·99 (16)	−0·28 (17)
O(4)	4·01 (24)	2·95 (21)	3·12 (20)	2·03 (19)	0·79 (18)	0·16 (17)

Table 8. *Observed and calculated structure factors for* CTASEL

H	10FO	10FC
K= 0 L= 0		
2	1652	2362
4	750	775
6	1238	1193
8	766	710
10	138	125
12	73	51
K= 1 L= 0		
1*	25	101
2	520	553
3	103	133
4	494	512
5	110	102
6	929	906
7	138	124
8	947	919
9	139	94
10	553	550
11	26	6
12	439	459
K= 2 L= 0		
0	1344	-2135
1	126	-116
2	1508	-1963
3	231	222
4	1463	-1532
5	185	150
6	822	-822
7	344	-349
8	385	-380
9	213	-212
10	216	-222
11*	34	19
12	84	-67
K= 3 L= 0		
1	280	221
2	468	-432
3	907	-873
4	687	-719
5	287	-277
6	506	-532
7	82	93
8	415	-415
9	166	-184
10	441	-453
11	226	-241
12	377	-385
K= 4 L= 0		
0	284	341
1	65	81
2	771	848
3	9	12
4	835	892
5	213	197
6	328	338
7	371	378
8	166	167
9	188	184
10	84	88
11	48	49
12*	52	-47
K= 5 L= 0		
1	332	290
2*	23	29
3	217	189
4	243	240
5*	33	-17
6	109	90
7	54	35
8	74	69
9	180	186
10	224	230
11	255	259
12	169	165
K= 6 L= 0		
0	257	269
1*	36	-27
2	133	126
3	250	-262
4	101	87
5	375	-378
6	127	135
7	206	-215
8	60	66
9	194	-204
10	71	81
11	216	-216
K= 7 L= 0		
1	113	-102
2	207	216
3	370	387
4	201	202
5	117	134
6	196	195
7	180	-191
8	140	132
9	110	-114
10	57	52
11	111	-105
K= 8 L= 0		
0	830	-849
1	100	92
2	658	-661
3	248	252
4	455	-467
5	238	242
6	434	-434
7	219	220
8	278	-292
9	309	310
10	96	-93
K= 9 L= 0		
1	405	-407
2	130	-142
3	231	-248
4	335	-337
5	106	-119
6	313	-339
7*	47	-89
8	263	-264
9*	22	2
K= 10 L= 0		
0	723	717
1*	39	-32
2	820	810
3	161	-159
4	719	722
5	243	-263
6	359	361
7	249	-249
8	202	201
K= 11 L= 0		
1	349	340
2	195	199
3	343	338
4	277	276
5	230	229
6	273	274
7	124	111
K= 12 L= 0		
0	566	-592
1	48	58
2	585	-581
3	140	139
4	462	-486
5	162	156
K= 13 L= 0		
1	272	-264
2	106	-108
K= 0 L= 1		
1	208	-229
-1*	31	58
3	638	-555
-3	255	237
5	511	-514
-5	5	5
7	313	-307
-7	124	113
9	177	-172
-9	343	339
11	88	-85
-11	276	271
-13	82	75
K= 1 L= 1		
0	132	176
1	128	212
-1	171	276
2*	10	29
-2*	17	-36
3	554	522
-3	600	500
4	105	78
-4	63	-43
5	79	82
-5	314	-247
6	312	288
-6	111	-85
7	347	-331
-7	435	-408
8	270	270
-8	286	-275
9	302	-299
-9	240	-249
10	203	196
-10	278	-275
11	215	-225
-11	175	-179
12	136	150
-12	147	-150
-13	214	-226
K= 2 L= 1		
0	974	-1181
1	311	357
-1	113	67
2	379	-440
-2	1226	-1390
3	456	510
-3	190	-198
4	411	-413
-4	891	-857
5	438	445
-5	227	-216
6	416	-406
-6	722	-700
7	240	239
-7	217	-203
8	228	-204
-8	557	-537
9	133	144
-9	216	-219
10	68	-68
-10	245	-239
11	91	73
-11	201	-210
12*	39	-10
-12	124	-122
-13	124	-130
K= 3 L= 1		
0	162	-219
1	588	-618
-1	315	-306
2	346	-361
-2	13	4
3	103	-167
-3	224	125
4	552	-573
-4	317	312
5*	40	-23
-5	50	-56
6	585	-600
-6	439	436
7*	38	-42
-7	125	-112
8	540	-545
-8	600	585
9	129	143
-9	47	75
10	544	-549
-10	586	600
11	269	275
-11	200	203
12	393	-411
-12	379	407
K= 4 L= 1		
0	564	652
1	165	-177
-1	186	-165
2	1147	1171
-2	1597	1596
3	349	-357
-3	46	-19
4	1112	1132
-4	1798	1869
5	298	-295
-5	365	353
6	494	453
-6	1016	1034
7	152	-142
-7	270	262
8	232	217
-8	615	604
9	132	-123
-9	85	95
10	195	185
-10	507	515
11	87	-94
-11	139	153
-12	227	241
K= 5 L= 1		
0	289	244
1	265	275
-1	75	92
2	648	657
-2	98	-73
3	354	343
-3	381	366
4	782	805
-4	504	-478
5*	34	112
-5	362	366
6	660	632
-6	707	-655
7*	46	14
-7	112	105
8	648	637
-8	669	-619
9*	44	20
-9	47	75
10	672	677
-10	614	-604
11*	43	-9
-11	62	60
-12	502	-500
K= 6 L= 1		
0	1211	-1253
1	136	126
-1	59	71
2	1093	-1124
-2	1245	-1244
3	3	1
-3	66	59
4	683	-698
-4	1273	-1253
5*	24	14
-5*	26	-8
6	560	-531
-6	1182	-1101
7	212	190
-7	180	-173
8	359	-353
-8	783	-739
9	156	165
-9	196	-195
10*	42	-28
-10	346	-352
11	72	69
-11	115	-115
K= 7 L= 1		
0	230	-196
1	294	-302
-1	539	-536
2	367	-379
-2*	36	-27
3	76	86
-3	157	-150
4	574	-581
-4	373	347
5	125	-120
-5	206	-174
6	663	-665
-6	624	581
7	242	-252
-7	384	-369
8	622	-631
-8	539	507
9	118	-119
-9	193	-196
10	485	-493
-10	443	439
-11	65	-64
K= 8 L= 1		
0	985	985
1	53	-45
-1	71	-72
2	710	716
-2	889	890
3	157	157
-3	65	-55
4	407	408
-4	752	717
5	60	47
-5	76	-71
6	310	303
-6	643	609
7	143	-136
-7	82	83
8	153	157
-8	429	425
9	46	-47
-9	126	110
-10	209	199
K= 9 L= 1		
0	111	110
1	57	47
-1	180	160
2	208	209
-2	74	-66
3*	27	22
-3	105	114
4	289	290
-4	152	-157
5	170	180
-5	192	190
6	458	464
-6	266	-267
7	186	196
-7	251	257
8	430	440
-8	357	-349
9	145	148
-9	167	167
K= 10 L= 1		
0	416	-412
1*	47	-38
-1*	67	-4
2	228	-231
-2	387	-372
3*	45	-52
-3*	45	24
4	172	-165
-4	206	-198
5	56	-77
-5*	45	45
6	115	-100
-6	188	-165
7	127	-119
-7	81	67
8	55	30
-8	127	-119
K= 11 L= 1		
0	54	-40
1	173	164
-1	217	207
2	147	-129
-2	124	129
3	128	-129
-3	106	-97
4	86	-91
-4	68	70
5	98	-108
-5	127	-125
6	153	-153
-6*	48	47
-7	82	22
K= 12 L= 1		
0*	25	-7
1	87	75
-1	69	62
2	73	-76
-2	108	-105
3	65	64
-3*	42	-15
4	89	-84
-4	163	-162
5	174	169
-5	111	-104
K= 13 L= 1		
0	62	-51
1	127	-126
-1	180	-172
-2*	49	-14
K= 0 L= 2		
0	2390	-2753
2	1104	-1069
-2	1739	-2040
4	744	-702
-4	623	-663
6	674	-625
-6	1231	-1176
8	249	-224
-8	1298	-1226
10*	47	43
-10	571	-531
-12	280	-278
K= 1 L= 2		
0	862	-1006
1	367	-336
-1	165	185
2	788	-949
-2	275	-287
3	76	-87
-3	533	470
4	1076	-1080
-4	169	141
5	79	-83
-5*	5	2
6	1362	-1351
-6	310	291
7	213	-216
-7	175	-139
8	976	-939
-8	629	600
9	85	-65
-9*	40	-55
10	493	-499
-10	668	645
11*	42	17
-11*	41	-38
-12	530	546
-13	66	-75
K= 2 L= 2		
C	1008	1214
1*	34	34
-1	217	228
2	1108	1209
-2	1201	1291
3	322	-324
-3	101	-80
4	954	949
-4	1319	1269
5	25	38
-5	41	15
6	399	389
-6	1056	1012
7	166	163
-7	106	-99
8	76	75
-8	756	742
9	70	-67
-9	239	-229
10*	9	-2
-10	563	551
11	86	-75
-11	87	-67
-12	331	335
-13*	4	2
K= 3 L= 2		
0	381	434
1	32	33
-1	711	-709
2	947	1018
-2	107	121
3	513	537
-3	13	-19
4	895	923
-4	66	-66
5	296	284
-5	120	113
6	574	587
-6	374	-376
7	182	189
-7	204	-208
8	512	522
-8	443	-434
9	181	201
-9	59	71
10	428	440
-10	390	-396
11	174	181
-11	291	303
-12	365	-394
-13	160	172
K= 4 L= 2		
0	414	-452
1	251	-264
-1	295	-269
2	648	-692
-2	358	-394
3	74	63
-3	115	113
4	366	-378
-4	724	-747
5*	22	-20
-5	247	231
6	191	-156
-6	630	-622
7	94	-106
-7	296	299
8	49	-39
-8	342	-319
9	36	38
-9	201	212
10	92	95
-10	262	-260
11	73	63
-11	63	61
-12	136	-145
K= 5 L= 2		
0	123	-111
1	97	114
-1	154	171
2	340	-370
-2	119	-79
3	203	-190
-3	25	42
4	288	-283
-4	88	40
5	231	-234
-5	347	298
6	59	-44
-6	209	186
7	214	-209
-7	190	193
8	119	-118
-8	139	132
9	275	-276
-9	124	-129
10	163	-156
-10	161	156
11	274	-276
-11	231	-230
-12	171	180
K= 6 L= 2		
0	98	-104
1	200	221
-1	27	25
2	156	-145
-2	20	5
3	314	320
-3*	9	-4
4	189	-188
-4	97	104
5	96	94
-5	239	-228
6	77	-95
-6	91	-52
7*	26	24
-7	318	-299
8*	44	-35
-8	120	-116
9	103	102
-9	174	-168
10	86	-75
-10	68	-70
-11	148	-144
K= 7 L= 2		
0	208	-180
1	87	-93
-1	97	-83
2	266	-270
-2*	36	43
3	162	-158
-3	482	-472
4	191	-187
-4*	38	17
5	94	97
-5	417	-417
6	229	-236
-6*	42	33
7	239	248
-7	60	38
8	248	-246
-8	92	89
9	221	226
-9	56	65
-10	69	35
-11*	94	-6
K= 8 L= 2		
0	705	680
1	156	-156
-1	14	6
2	501	512
-2	406	374
3	286	-298

Table 8 (*cont.*)

H	10FO	10FC
-3	41	30
4	281	286
-4	328	304
5	208	-202
-5	58	68
6	286	290
-6	565	540
7	177	-171
-7	128	125
8	140	144
-8	450	433
9	202	-210
-9	229	217
-10	195	199
K# 9 L# 2		
0	216	200
1	239	253
-1	394	395
2	374	380
-2	119	116
3	86	100
-3	380	378
4	483	473
-4*	42	8
5*	47	25
-5	230	226
6	449	449
-6	159	-150
7*	44	-14
-7	158	147
8	393	389
-8	182	-175
-9	122	110
K# 10 L# 2		
0	541	-524
1	79	76
-1	102	102
2	547	-559
-2	668	-661
3	211	209
-3*	43	28
4	436	-449
-4	749	-752
5	321	323
-5	103	-90
6	194	-194
-6	494	-496
7	239	239
-7	105	-93
-8	328	-322
K# 11 L# 2		
0	219	-217
1	239	-239
-1	244	-250
2	416	-413
-2	70	-82
3	274	-277
-3	317	-321
4	484	-487
-4*	1	0
5	142	-143
-5	238	-238
6	419	-411
-6	99	95
-7	162	-164
K# 12 L# 2		
0	441	447
1	119	-121
-1	52	-62
2	373	362
-2	578	578
3	152	-179
-3*	1	0
4	306	303
-4	551	558
-5*	51	28
K# 13 L# 2		
-1	192	192
K# 0 L# 3		
1	317	-296
-1	355	-253
3	442	419
-3	82	26
5	513	489
-5	91	-56
7	129	129
-7	167	-144
9	127	114
-9	349	-335
11	94	73
-11	422	-419
-13	199	-203
K# 1 L# 3		
0	238	-238
1	411	415
-1	468	411
2	176	-202
-2	329	-292
3	58	33
-3	445	-435
4	414	-395
-4	38	-38
5	238	228

H	10FO	10FC
-5	152	-177
6	308	-280
-6*	32	-34
7	349	343
-7	105	104
8	129	-130
-8	17	3
9	265	267
-9	86	-90
10	118	-115
-10	169	166
11	259	251
-11	67	-75
-12	149	155
-13	129	140
K# 2 L# 3		
0	681	726
1	111	-142
-1	82	-42
2	388	408
-2	1194	1239
3	257	-300
-3	80	66
4	232	238
-4	1125	1116
5	294	-289
-5	202	171
6	115	101
-6	582	554
7	172	-186
-7	222	216
8	65	65
-8	473	446
9	140	-131
-9	276	282
10*	49	-48
-10	357	361
11	79	-25
-11	282	291
-12	188	194
-13	185	198
K# 3 L# 3		
0	567	605
1	238	246
-1	165	174
2	756	803
-2	625	635
3	205	-188
-3	248	-232
4	893	935
-4	254	231
5	142	-148
-5	103	123
6	537	536
-6	64	-60
7	92	-95
-7	409	417
8	317	325
-8	182	-171
9	235	-235
-9	157	152
10	357	357
-10	338	-342
-11	67	-64
-12	316	-324
-13	53	-48
K# 4 L# 3		
0	833	-856
1	417	420
-1	176	192
2	779	-915
-2	1438	-1390
3	240	229
-3*	21	10
4	590	-576
-4	1700	-1649
5	132	139
-5	140	-133
6	95	-83
-6	943	-951
7	212	213
-7	270	-269
8*	49	35
-8	614	-605
9	133	125
-9	144	-149
10	87	62
-10	624	-636
-11	92	-82
-12	397	-416
K# 5 L# 3		
0	881	-899
1	229	-235
-1	201	-222
2	1090	-1116
-2	504	-556
3	110	-103
-3	232	-224
4	852	-844
-4	267	-231
5*	21	2
-5	412	-376
6	574	-550
-6	150	118
7	98	98
-7	279	-270

H	10FO	10FC
8	519	-515
-8	337	316
9	63	62
-9	98	-108
10	433	-428
-10	344	342
-11	84	-98
-12	336	340
K# 6 L# 3		
0	1131	1226
1	266	-272
-1	174	-170
2	748	750
-2	1115	1095
3	140	-132
-3*	38	-31
4	295	290
-4	1053	992
5	148	-149
-5*	44	-33
6	181	188
-6	1100	1095
7	206	-207
-7*	43	45
8*	7	1
-8	888	855
9	71	-84
-9	46	67
-10	464	464
-11*	46	28
K# 7 L# 3		
0	706	712
1	199	200
-1	476	475
2	713	707
-2	450	442
3	38	22
-3	336	331
4	585	583
-4	156	146
5	95	94
-5	192	181
6	590	607
-6	140	-117
7	117	113
-7	258	246
8	494	503
-8	229	-229
9	87	90
-9	148	154
-10	248	-246
-11	60	43
K# 8 L# 3		
0	711	-710
1	81	88
-1	196	180
2	412	-416
-2	728	-729
3*	36	22
-3	90	55
4	185	-186
-4	713	-684
5	127	126
-5	41	28
6	76	-59
-6	703	-682
7	93	94
-7	76	79
8	82	54
-8	532	-519
-9	52	46
-10	306	-306
K# 9 L# 3		
0	303	-314
1	127	-130
-1	205	-196
2	279	-293
-2	218	-223
3	130	-143
-3	175	-185
4	357	-354
-4	85	-92
5	158	-153
-5	84	-98
6	392	-413
-6*	40	18
7	147	-150
-7	67	-84
-8	136	139
-9	93	-86
K# 10 L# 3		
0	156	170
1*	44	17
-1*	10	-3
2	104	104
-2	309	301
3*	30	-22
-3	51	-47
4	99	103
-4	260	255
5	67	47
-5	66	-56
6*	49	-19
-6	179	174
-7	96	-83

H	10FO	10FC
-8	184	186
K# 11 L# 3		
0	86	84
1*	22	-1
-1	87	-96
2	53	66
-2*	43	12
3	170	162
-3*	32	28
4	75	68
-4*	44	-5
5	141	134
-5*	17	11
-6*	47	21
-7	122	-112
K# 12 L# 3		
0	68	50
1	97	-89
-1	136	-131
2	74	77
-2	130	113
-3	74	-29
-4	181	165
K# 0 L# 4		
0	1015	941
2	434	371
-2	1278	1264
4	80	72
-4	1261	1246
6*	11	4
-6	1426	1421
8	100	-89
-8	1379	1337
10	236	-221
-10	819	807
-12	435	452
K# 1 L# 4		
0	774	840
1	193	154
-1	125	120
2	701	698
-2	865	821
3	47	-43
-3	326	-280
4	854	821
-4	441	424
5	104	107
-5	94	-86
6	843	816
-6	191	176
7	142	143
-7	225	206
8	576	561
-8	45	-34
9*	37	11
-9	95	94
10	338	335
-10	314	-300
-11*	120	-10
-12	383	-394
-13	96	96
K# 2 L# 4		
0	535	-566
1	25	-34
-1	134	-134
2	417	-435
-2	987	-958
3	166	-158
-3	103	-34
4	234	-227
-4	1217	-1189
5	168	-181
-5	117	115
6	79	74
-6	1172	-1138
7*	62	-20
-7	47	48
8	178	184
-8	935	-944
9	95	76
-9	64	63
10	168	167
-10	724	-733
-11	122	122
-12	461	-481
-13	107	99
K# 3 L# 4		
0	596	-647
1	19	-11
-1	151	176
2	674	-702
-2	430	-435
3	186	-196
-3*	34	24
4	506	-518
-4	358	-347
5	232	-239
-5	146	-150
6	416	-431
-6	121	-112
7	174	-179
-7*	27	-32
8	370	-377
-8	187	178

H	10FO	10FC
9	138	-131
-9	55	-62
10	273	-267
-10	201	220
-11	184	-195
-12	176	195
K# 4 L# 4		
0	390	412
1	349	377
-1	389	379
2	198	194
-2	443	455
3	149	144
-3	57	-38
4	52	55
-4	445	451
5	106	128
-5	191	-184
6*	46	-32
-6	587	572
7	64	80
-7	125	-128
8	148	-156
-8	494	482
9	97	-83
-9	156	-162
-10	309	322
-11	147	-164
-12	205	223
K# 5 L# 4		
0	217	222
1	64	-72
-1	199	-197
2	283	296
-2	80	65
3	172	165
-3	106	93
4	163	168
-4	67	64
5	196	204
-5*	27	72
6	113	117
-6*	34	9
7	233	236
-7	100	-108
8	121	110
-8	77	-73
9	237	234
-9*	28	25
-10	65	-66
-11	147	141
-12	85	-76
K# 6 L# 4		
0*	15	-1
1	393	-401
-1	251	-244
2	56	91
-2*	18	3
3	272	-276
-3	71	-69
4	116	127
-4	122	-18
5	122	-133
-5*	24	10
6*	44	50
-6	63	44
7*	51	-64
-7	192	180
8*	49	31
-8	145	148
-9	226	224
-10	96	111
-11	151	154
K# 7 L# 4		
0	303	307
1*	29	-16
-1	76	68
2	147	142
-2	158	155
3*	35	-22
-3	224	221
4*	31	24
-4	57	70
5	130	-123
-5	221	221
6	156	167
-6	106	101
7	227	-235
-7	58	52
8	205	193
-8*	45	-23
-9*	41	30
-10	77	-70
-11	109	103
K# 8 L# 4		
0	389	-409
1	268	279
-1	139	136
2	147	-157
-2	366	-346
3	320	330
-3	128	130
4	79	-88
-4	233	-236
5	188	195

H	10FO	10FC
-5	93	99
6	118	-108
-6	551	-538
7	97	97
-7	62	-56
-8	555	-581
-9	178	-170
-10	264	-274
K# 9 L# 4		
0	351	-358
1*	44	-66
-1	158	-165
2	327	-339
-2	286	-294
3	55	42
-3	250	-253
4	334	-336
-4	210	-224
5	58	61
-5	272	-271
6	358	-356
-6	109	-93
-7	199	-205
-8*	50	50
-9	162	-166
K# 10 L# 4		
0	276	273
1	146	-145
-1	179	-181
2	226	224
-2	460	473
3	256	-260
-3	224	-222
4	151	154
-4	668	665
5	232	-231
-5	62	-57
-6	589	585
-7*	50	33
-8	427	419
K# 11 L# 4		
0	284	293
1	126	116
-1	95	52
2	431	441
-2	259	256
3	127	120
-3	242	241
-4	237	247
-5	289	282
-6	90	100
K# 12 L# 4		
0	245	-253
-1	158	153
-2	411	-416
K# 0 L# 5		
1	89	-71
-1	65	47
3	379	-349
-3	395	-420
5*	33	-29
-5	243	-279
7	150	140
-7*	36	90
9	69	24
-9	143	136
-11	218	210
K# 1 L# 5		
0*	34	135
1	152	-156
-1	155	-137
2	333	339
-2	102	135
3	192	-190
-3	343	349
4	326	328
-4	183	171
5	257	-249
-5	528	523
6	165	167
-6	64	65
7	208	-202
-7	145	131
8	114	110
-8	61	66
9	227	-217
-9	74	77
-10*	16	1
-11	142	141
-12	101	-106
K# 2 L# 5		
0	274	-283
1	179	200
-1	239	255
2	117	-123
-2	314	-314
3	121	121
-3	292	285
4	78	71
-4	589	-571
5*	32	24
-5	125	137
6*	37	14

Table 8 (*cont.*)

H	10FO	10FC
-6	520	-494
7*	5	-1
-7	38	-22
8	60	42
-8	329	-318
9	56	-19
-9	114	-125
-10	368	-377
-11	191	-199
-12	329	-342

K# 3 L# 5

0	448	-445
1	58	-40
-1	245	-250
2	769	-814
-2	451	-458
3	183	182
-3	85	-76
4	723	-758
-4	505	-490
5	150	160
-5	93	-96
6	368	-363
-6	174	-161
7	153	167
-7	321	-332
8	264	-268
-8*	39	-36
-9	224	-230
-10	47	40
-11*	22	13
-12	175	187

K# 4 L# 5

0	339	330
1	248	-251
-1	384	-390
2	297	291
-2	586	548
3*	22	-19
-3	137	-136
4	74	61
-4	914	845
5	108	-107
-5	42	-38
6	156	-150
-6	648	633
7	114	-120
-7*	44	-19
8	200	-198
-8	512	518
-9	85	77
-10	664	704
-11	81	79
-12	547	589

K# 5 L# 5

0	766	816
1	58	50
-1	144	144
2	835	845
-2	673	642
3	60	69
-3	183	174
4	683	685
-4	503	448
5	67	-57
-5	132	131
6	512	505
-6	257	235
7	180	-172
-7	199	188
8	385	375
-8	35	16
-9	153	157
-10	119	-130
-11	99	88

K# 6 L# 5

0	493	-499
1	176	188
-1	171	165
2	140	-153
-2	611	-595
3	130	130
-3*	31	15
4*	46	34
-4	539	-500
5	175	174
-5	54	56
6	125	123
-6	709	-682
7	145	142
-7	89	91
-8	838	-827
-9*	46	18
-10	601	-610
-11*	47	8

K# 7 L# 5

0	733	-743
1	93	-109
-1	161	-177
2	570	-578
-2	564	-572
3	45	-45
-3	103	-106
4	496	-508
-4	294	-285

H	10FO	10FC
5*	46	-39
-5	69	-69
6	486	-499
-6	194	-187
-7	144	-142
-8	52	-59
-9	93	-96
-10	109	97

K# 8 L# 5

0	222	230
1	67	-69
-1*	39	-38
2	80	73
-2	349	352
3	120	-114
-3*	4	-1
4*	49	-43
-4	445	436
5	141	-141
-5*	36	-15
6	146	-140
-6	573	569
-7	98	-83
-8	560	560
-9	98	-105

K# 9 L# 5

0	343	358
1	124	131
-1	76	72
2	315	331
-2	312	312
3	104	110
-3*	35	20
4	320	316
-4	209	215
5	110	96
-5*	26	9
-6	108	121
-7*	81	-16
-8*	43	5

K# 10 L# 5

0*	15	-5
1*	53	-40
-1	78	-84
2	67	18
-2	132	-135
3	67	46
-3*	7	-3
-4	248	-243
-5*	42	20
-6	246	-234
-7*	42	14

K# 11 L# 5

0	111	-110
1*	46	-33
-1*	56	38
-2	98	-86
-3*	35	12
-4	87	-60

K# 0 L# 6

0	375	-340
2	42	24
-2	521	-501
4	202	179
-4	671	-650
6	178	149
-6	956	-950
8	209	179
-8	883	-881
-10	540	-547
-12	407	-432

K# 1 L# 6

0	911	-969
1	79	-65
-1	149	-145
2	755	-758
-2	986	-924
3*	33	-11
-3	18	-5
4	542	-529
-4	745	-712
5	73	-69
-5	92	96
6	413	-395
-6	492	-492
7	100	-81
-7*	21	-6
-8	269	-268
-9*	41	-36
-10*	44	-41
-11	61	51
-12	140	137

K# 2 L# 6

0	157	164
1*	35	37
-1	86	-82
2	57	54
-2	466	437
3	69	69
-3	90	-84
4	86	-75
-4	681	655
5*	57	17

H	10FO	10FC
-5*	37	-23
6	210	-208
-6	687	665
7*	33	-8
-7*	41	-18
-8	593	602
-9*	39	-19
-10	525	553
-11*	48	-52
-12	419	453

K# 3 L# 6

0	581	611
1	82	89
-1	72	59
2	458	481
-2	661	659
3	167	174
-3	130	125
4	359	368
-4	530	525
5	155	173
-5*	33	31
6	245	244
-6	343	331
7	164	157
-7	143	-135
-8	106	111
-9	84	-86
-10*	50	-34
-11*	1	0

K# 4 L# 6

0	75	-97
1	68	-77
-1	124	-130
2*	28	5
-2	257	-268
3*	29	26
-3	53	46
4	54	56
-4	255	-256
5*	52	-50
-5	81	81
6	132	125
-6	231	-217
7	66	-45
-7*	59	-16
-8	313	-317
-9	42	41
-10	314	-334
-11	147	152

K# 5 L# 6

0	139	-151
1	117	-111
-1*	36	-18
2	136	-129
-2	151	-156
3	166	-175
-3*	32	-35
4	111	-120
-4	114	-119
5	245	-227
-5*	31	-39
6	97	-79
-6	85	-88
-7	146	138
-8*	46	-33
-9	209	193
-10*	49	35
-11	88	87

K# 6 L# 6

0*	40	-14
1	89	97
-1	151	153
2*	46	-51
-2	50	-60
3	81	97
-3	101	116
4	50	-61
-4	49	-74
5	102	98
-5*	46	50
6*	8	1
-6*	43	-41
-7*	19	-5
-8*	47	-42
-9	102	-97
-10*	48	-37

K# 7 L# 6

0	304	-306
1	141	150
-1	59	63
2	101	-105
-2	283	-280
3	95	125
-3	143	-138
4	72	-60
-4	117	-117
5	186	187
-5	161	-158
-6	132	-122
-7	127	-124
-8	97	-91
-9	195	-204

K# 8 L# 6

H	10FO	10FC
0	157	156
1	195	-200
-1	124	-132
2*	36	7
-2	206	208
3	210	-215
-3	154	-156
4*	53	-25
-4	204	195
-5	163	-162
-6	273	278
-7	61	-50
-8	361	379

K# 9 L# 6

0	373	392
1	65	-53
-1	67	49
2	293	298
-2	407	415
-3	119	111
-4	304	305
-5	220	220
-6	208	209
-7	258	260

K# 10 L# 6

0	68	-72
-1	169	172
-2	231	-235
-3	231	225
-4	391	-392

K# 0 L# 7

1	329	306
-1	136	129
3	278	250
-3	208	216
5*	37	-19
-5	240	244
-7	60	-52
-9	129	-129
-11	56	-56

K# 1 L# 7

0	176	-160
1	201	210
-1	111	113
2	192	-180
-2	95	-88
3	257	256
-3*	5	0
4	102	-101
-4	176	-163
5	181	180
-5	150	-144
6	89	-75
-6	177	-179
-7	106	-95
-8	107	-109
-9*	43	-47
-10	72	-72
-11	128	-133

K# 2 L# 7

0	79	82
1	213	-220
-1	243	-254
2	112	-93
-2	96	91
3	125	-121
-3	230	-228
4	96	-100
-4	164	157
5*	55	-21
-5	146	-138
6*	43	-29
-6	368	366
-7*	31	-16
-8	340	361
-9*	45	49
-10	269	287
-11	95	102

K# 3 L# 7

0	311	327
1	87	-92
-1*	28	4
2	396	422
-2	337	336
3	166	-179
-3*	23	6
4	289	300
-4	540	531
5	171	-175
-5*	36	16
-6	425	423
-7	113	114
-8	202	212
-9	152	161
-10	165	165

K# 4 L# 7

0*	42	-26
1	88	98
-1	262	262
2	60	39
-2	171	-167
3*	47	59
-3	229	219

H	10FC	10FC
4	138	123
-4	424	-402
5	81	80
-5	73	63
-6	455	-454
-7	69	71
-8	416	-430
-9	52	38
-10	515	-561

K# 5 L# 7

0	448	-458
1*	45	29
-1	71	63
2	397	-409
-2	570	-563
3*	45	-21
-3	78	-68
4	343	-337
-4	628	-592
-5	101	-84
-6	483	-461
-7	84	-72
-8	306	-303
-9	160	-159

K# 6 L# 7

0	75	68
1	76	-89
-1	121	-121
2	151	-77
-2	218	208
3	66	-67
-3	92	-60
4	180	-183
-4	318	299
-5	63	-65
-6	423	417
-7	140	-134
-8	560	562
-9	92	-74

K# 7 L# 7

0	438	468
1	55	31
-1	57	46
2	308	314
-2	519	532
3	62	39
-3*	42	15
-4	396	397
-5*	43	29
-6	351	342
-7	156	149
-8	316	312

K# 8 L# 7

0	56	10
1*	45	35
-1*	39	18
-2	106	-95
-3*	60	-25
-4	242	-234
-5	62	44
-6	361	-356

K# 9 L# 7

-1	67	-70
-2	272	-279
-3*	36	-6
-4	217	-232

K# 0 L# 8

0	120	-95
2	264	-237
-2	89	55
4	272	-245
-4	133	121
-6	345	353
-8	514	530
-10	391	406

K# 1 L# 8

0	566	599
1	62	55
-1	95	84
2	411	415
-2	576	548
3*	41	-11
-3*	41	18
4	285	270
-4	420	411
-5*	47	-21
-6	412	424
-7*	49	-39
-8	360	371
-9*	52	-26

K# 2 L# 8

0	119	121
1*	50	-43
-1	86	-66
2	154	162
-2*	43	-26
3	52	42
-3*	23	-6
4	218	209
-4	201	-199
-5	55	-64
-6	274	-274

H	10FC	10FC
-7	109	-109
-8	312	-326
-9*	57	-18

K# 3 L# 8

0	278	-297
1	102	-108
-1	84	-80
2	262	-278
-2	392	-385
3	79	-72
-3	70	-63
-4	407	-411
-5*	37	-13
-6	290	-298
-7	137	134
-8	193	-196
-9*	52	119

K# 4 L# 8

0	95	-57
1*	36	12
-1	157	149
2	108	-112
-2*	47	16
3	98	-81
-3	130	120
-4	97	100
-5	103	107
-6	117	110
-7	163	158
-8	154	154

K# 5 L# 8

0	64	57
1	115	104
-1	85	87
2	90	66
-2	112	120
-3*	44	33
-4	174	156
-5*	52	-33
-6	103	96
-7	98	-97
-8	67	68

K# 6 L# 8

0	61	9
1	46	-25
-1	113	-107
-2	52	43
-3	241	-237
-4*	49	50
-5	215	-208
-6	60	-10
-7	97	-103

K# 7 L# 8

-1	97	-99
-2	155	156
-3*	54	25
-4	82	73
-5	86	88

K# 0 L# 9

1	67	-73
-1	53	-45
-3	76	-69
-5	118	-130
-7	77	-88

K# 1 L# 9

0	133	136
1	161	-171
-1	109	-104
-2	146	137
-3	74	-47
-4	119	111
-5*	35	-5
-6	134	134
-7	67	61

K# 2 L# 9

0	83	74
1*	52	51
-1	95	79
-2*	50	20
-3	83	93
-4*	51	15
-5	100	112
-6	80	-89
-7	103	111

K# 3 L# 9

0	248	-258
-1	76	55
-2	322	-320
-3	73	51
-4	400	-396
-5*	55	-7
-6	360	-363

K# 4 L# 9

-1	79	-75
-2	80	-58
-3	151	-136
-4	92	70
-5	136	-125

and of one oxygen atom at 2·31 Å which forms the top. Also, the copper ion is located 0·2 Å above the plane of the base of the pyramid. Weak interactions at about 2·74 Å complete the sixth position about the copper ion.

The four nitrogen atoms about the copper ion are not arranged in a perfect square as can be noted by the departure from 90° and 180° of the nitrogen–copper–nitrogen angles (Table 9*a*). In addition, the water–copper–water link of the weak chemical chain is slightly bent.

The sulfur–oxygen separations [Table 9(*b*)] found in the SO_4^{2-} ion are in good agreement with similar values found in other sulfates (ITCX, Table 4·1·9, p. 272; Larson, 1965; Morosin & Smith, 1967).

A network of hydrogen bonds [Table 9(*c*)] interlace the sulfate ions and the weak copper-water-copper chains. This network is shown in Fig. 1. Mazzi previously pointed out the structural basis for the perfect cleavage (010) which has been observed in this complex. The observed electron density peaks which form the basis for assigning the hydrogen positional parameters (Table 1) lie off the line connecting the heavy atoms as has been observed in most hydrogen bonded systems. The corresponding angles as well as the separation from the heavy atom are listed in Table 9(*d*).

The average copper–nitrogen separations in CTASUL (2·031(6)Å) and in CTASEL (2·005(9)Å) (Table 10*a*) compare favorably with the reported values of 1.96 – 2·06 Å summarized by Brown & Lingafelter (1964). It appears that the copper–nitrogen separation decreases as the distance of the atoms filling the octahedral position increases. Examples of $Cu(NH_3)_4^{2+}$ complexes are CTASUL (2·031 Å Cu-N and 2.339 Å Cu – O), CTASEL (2·005 Å Cu–N and 2·451 Å Cu–O) and $Na_4[Cu(NH_3)_4]\,[Cu(S_2O_3)_2]_2$ (Ferrari, Braibanti, & Tiripicchio, 1966) (1·994 Å Cu–N and 5·76 Å for nearest atoms normal to plane of four nitrogen atoms). Similarly, values reported in ethylenediamine copper complexes are 2·04 Å Cu–N and 2·60 Å Cu–O in $Cu(en)_2(ClO_4)_2$ (Pajunen, 1967), 2·01 Å Cu–N and 2·59 Å Cu–O in $Cu(en)_2(NO_3)_2$ (Komiyama & Lingafelter, 1964), 1.98 Å Cu-N and 2.68 Å Cu-O in $[Cu(en)_2(H_2O)Cl]Cl$ (more recently 2·00 Å Cu–N and 2·62 Å Cu–O values have been reported in this compound by Ball, Hall, Rickard & Waters, 1967) and 1·97 Å Cu–N and 2.78 Å Cu–O in $[Cu(en)_2(H_2O(Br]Br$ (Mazzi, 1953).

The prominent feature in the structure of CTASEL is the –Cu–O–Se–O–Cu– chains formed along the *c* axis linking the selenate and $Cu(NH_3)_4^{2+}$ ions. The two Cu–O separations (2·451 and 2·607 Å, Table 10) are

Table 9. *Interatomic separation and angles in* $Cu(NH_3)_4SO_4.H_2O$

(*a*) those which involve the copper octahedron

Cu—N(1)	2·031 (6) Å	N(1)–Cu–N(1*m*)	91·83 (24)°
Cu—N(2)	2·032 (6)	N(1)–Cu–N(2)	86·90 (24)
Cu—O(1)	2·339 (9)	N(2)–Cu–N(2*m*)	93·25 (24)
Cu—O(1*a*)	3·475 (9)	N(1)–Cu–O(1)	96·63 (28)
O(1)–N(1)	3·270 (10)	N(2)–Cu–O(1)	91·44 (28)
O(1)–N(2)	3·136 (10)	N(1)–Cu–N(2*m*)	171·93 (24)
		O(1)–Cu–O(1*a*)	174·48 (30)

(*b*) those which involve sulfate ion

S —O(2)	1·461 (6) Å	O(2)–S–O(2*m*)	109·98 (30)°
S —O(3)	1·455 (7)	O(2)–S–O(3)	111·10 (33)
S —O(4)	1·471 (6)	O(2)–S–O(4)	108·01 (32)
O(2)–O(2*m*)	2·393 (8)	S(3) –S–O(4)	108·53 (34)
O(2)–O(3)	2·404 (9)		
O(2)–O(4)	2·372 (8)		
O(3)–O(4)	2·375 (9)		

(*c*) those which involve hydrogen bond interactions

O(1)–O(2)	2·777 (9) Å	O(2)—O(1)–O(2*m*)	114·68 (40)°
N(1)–O(4)	2·978 (8)	O(4)—N(1)–O(4*a*)	93·32 (34)
N(1)–O(4*a*)	3·113 (8)	O(4)—N(1)–O(3*a*)	101·03 (34)
N(1)–O(3*a*)	3·134 (9)	O(4*a*)–N(1)–O(3*a*)	127·91 (34)
N(2)–O(2*b*)	3·008 (8)	O(2*a*)–N(2)–O(2*b*)	98·26 (32)
N(2)–O(2*a*)	3·032 (8)	O(2*a*)–N(2)–O(3)	98·00 (33)
N(2)–O(3)	3·183 (9)	O(2*b*)–N(2)–O(3)	121·97 (33)

(*d*) those which involve hydrogen atoms

O(1)–H(1)	0·86 Å	H(1)—O(1)–H(1*m*)	111°
O(2)–H(1)	1·93	O(1)—H(1)–O(2)	170
N(1)–H(2)	1·12	O(3*a*)–H(2)–N(1)	166
N(1)–H(3)	0·86	O(4*a*)–H(3)–N(1)	152
N(1)–H(4)	0·90	O(4)—H(4)–N(1)	173
N(2)–H(5)	0·93	O(3)—H(5)–N(2)	160
N(2)–H(6)	0·97	O(2*b*)–H(6)–N(2)	156
N(2)–H(7)	0·89	O(2*a*)–H(7)–N(2)	174

significantly different from each other; however, this difference is not so great as found in CTASUL.

There are few selenium–oxygen separations (ITCX, Table 4·1·9, p. 272) with which the present values may be compared. The average value of 1·635 Å may be taken as the most accurate selenium–oxygen value thus far available.

In CTASEL the selenate ions are part of the chain and no other constituents are present; thus, only the the chains need be held together by hydrogen bonds (Fig. 2). The shorter nitrogen–oxygen separations are listed in Table 10(*c*) together with the angles between these heavy atoms. Nitrogen atoms N(2) and N(3) each have three near-neighbor oxygen atoms as required by the available hydrogen atoms; on the other hand, N(1) and N(3) have a more complex environment. Two of the four near-neighbor oxygen atoms for N(1) are at separations (2.71 and 2·76 Å) which are

Table 10. *Interatomic separations and angles in* $Cu(NH_3)_4SeO_4$

(*a*) those which involve the copper octahedron

Cu–N(1)	2·017 (9) Å	O(2*a*)–Cu–N(1)	88·10 (29)°
Cu–N(2)	2·012 (9)	O(2*a*)–Cu–N(2)	87·34 (29)
Cu–N(3)	1·992 (9)	O(2*a*)–Cu–N(3)	91·24 (29)
Cu–N(4)	2·000 (9)	O(2*a*)–Cu–N(4)	91·95 (29)
Cu–O(1)	2·607 (7)	N(1)—Cu–N(2)	88·57 (30)
Cu–O(2*a*)	2·451 (8)	N(1)—Cu–N(3)	88·97 (30)
		O(1)—Cu–N(1)	92·15 (29)
		N(4)—Cu–N(4)	91·44 (30)
		N(2)—Cu–O(1)	89·94 (29)
		N(3)—Cu–N(4)	91·01 (30)
		N(3)—Cu–O(1)	91·49 (29)
		N(4)—Cu–O(1)	87·81 (29)
		O(2*a*)–Cu–O(1)	177·27 (27)
		N(1)—Cu–N(4)	179·95 (30)
		N(2)—Cu–N(3)	177·20 (30)

(*b*) those which involve the selenate ion

Se—O(1)	1·647 (8) Å	O(1)-Se–O(2)	108·82 (33)°
Se—O(2)	1·626 (8)	O(1)-Se–O(3)	109·04 (33)
Se—O(3)	1·638 (8)	O(1)-Se–O(4)	109·76 (33)
Se—O(4)	1·629 (8)	O(2)-Se–O(3)	109·95 (33)
O(1)–O(2)	2·662 (11)	O(2)-Se–O(4)	109·59 (33)
O(1)–O(3)	2·675 (11)	O(3)-Se–O(4)	109·65 (33)
O(1)–O(4)	2·680 (11)		
O(2)–O(3)	2·673 (11)		
O(2)–O(4)	2·660 (11)		
O(3)–O(4)	2·671 (11)		

(*c*) those which involve hydrogen bond interactions

N(1)–O(1*a*)	2·757 (11) Å	O(1*a*)–N(1)–O(3*a*)	105·63 (51)°
N(1)–O(3*a*)	2·712 (12)		
N(2)–O(2*b*)	3·114 (12)	O(2*b*)–N(2)–O(3*b*)	88·73 (53)
N(2)–O(3*b*)	3·356 (12)	O(2*b*)–N(2)–O(4*b*)	106·21 (53)
N(2)–O(4*b*)	3·099 (12)	O(3*b*)–N(2)–O(4*b*)	81·28 (53)
N(3)–O(4)	2·944 (12)	O(4)—N(3)–O(1*b*)	100·57 (53)
N(3)–O(1*b*)	3·104 (11)	O(4)—N(3)–O(3*c*)	103·00 (51)
N(3)–O(3*c*)	3·206 (12)	O(1*b*)–N(3)–O(3*c*)	87·29 (53)
N(4)–O(3*d*)	3·033 (12)	O(3*d*)–N(4)–O(2*c*)	94·92 (53)
N(4)–O(2*c*)	3·108 (12)	O(3*d*)–N(4)–O(4*c*)	88·51 (53)
N(4)–O(4*c*)	2·990 (12)	O(2*c*)–N(4)–O(4*c*)	109·18 (53)
N(1)–O(2*b*)	3·720 (12)		
N(1)–O(1*b*)	3·886 (11)		
N(3)–O(3*a*)	3·440 (12)		

(*d*) those which involve hydrogen atoms

N(1)–H(1)	0·69 Å	N(1)–H(1)—O(1*a*)	156°
N(1)–H(2)	0·56	N(1)–H(2)—O(3*a*)	124
N(1)–H(3)	0·71		
N(2)–H(4)	0·93	N(2)–H(4)—O(2*b*)	171
N(2)–H(5)	0·99	N(2)–H(5)—O(3*b*)	134
N(2)–H(6)	0·99	N(2)–H(6)—O(4*b*)	163
N(3)–H(7)	1·07	N(3)–H(7)—O(4)	163
N(3)–H(8)	1·15	N(3)–H(8)—O(1*b*)	129
N(3)–H(9)	0·90	N(3)–H(9)—O(3*c*)	144
N(4)–H(10)	0·95	N(4)–H(10)–O(3*d*)	168
N(4)–H(11)	0·98	N(4)–H(11)–O(2*c*)	159
N(4)–H(12)	0·97	N(4)–H(12)–O(4*c*)	158

among the shortest of their kind found in either copper tetrammine compound while the remaining two are at separations over 3·7 Å Such large separations are even greater than the typical bifurcated hydrogen bonds found in several hydrates (separations summarized by Morosin, 1967) and, hence, do not appear to be involved in the hydrogen bonding network. There are three near-neighbor oxygen atoms for N(3) which are at typical interatomic separations; however, there is an additional near-neighbor oxygen atom at 3·44 Å. When the spatial arrangement of the near-neighbor oxygen atoms is considered, this latter oxygen atom can be eliminated from the possibility of being involved in the hydrogen bonding network. As was the case for CTASUL, the observed hydrogen positions lie off the lines connecting these atoms as can be seen from the angles listed in Table 10(*d*).

The anisotropic thermal parameters in these copper tetrammine compounds are compatible with the strong bonding which occurs along particular directions. For example, the magnitude of the nitrogen thermal parameters perpendicular to the square plane formed by the copper and nitrogen atoms is significantly larger than those parallel to this plane. Similarly, oxygen atoms constrained by chemical bonds to the sulfur, selenium or copper atoms have thermal parameters which are smaller parallel to, rather than perpendicular to, the bond directions.

The thermal and magnetic properties of CTASEL are being investigated and will be reported elsewhere.

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The Crystal Structure of Bis-L-histidinecopper(II) Dinitrate Dihydrate

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The crystal structure of bis-L-histidinecopper(II) dinitrate dihydrate has been determined and refined using three-dimensional X-ray data. The crystals were prepared by crystallization from a solution of pH = 3·7 containing copper(II) ions and histidine molecules in the ratio 1:2 and $NaNO_3$ in large excess. The crystals are triclinic and belong to space group $P\bar{1}$. The unit cell contains one formula unit and has the dimensions $a = 5{\cdot}458_2$, $b = 7{\cdot}153_3$, $c = 13{\cdot}844_4$ Å, $\alpha = 98{\cdot}61_7°$, $\beta = 87{\cdot}07_0°$ and $\gamma = 109{\cdot}83_0°$. The intensity data were treated by Fourier methods and by least-squares refinement. The anisotropic refinement converged to $R = 7{\cdot}6\%$ using 1813 independent reflexions. Two histidine molecules coordinate to a central copper atom, each through the amino nitrogen and a carboxylate oxygen. The imidazole groups are not coordinated to the copper atom and turn away from it. The coordination about copper is square planar with the four donor atoms situated 1·93–2·00 Å from the copper. There are two water molecules, one above and one below this plane, at distances of 2·46 and 2·78 Å. The nitrate ions are situated between the imidazole rings. The structure is linked together by an extensive hydrogen bond network.

Introduction

Crystal structure investigations of biochemically interesting metal complexes have been started in conjunction with the Department of Biochemistry at this University. In this paper the results of the structure determination of bis-L-histidinecopper(II) dinitrate dihydrate are presented.

In metal activated enzymes, histidyl residues are known to be important metal binding sites. Owing to