ACTA CHEMICA SCANDINAVICA 26 (1972) 3969–3976

Metal Complexes with Mixed Ligands

4. The Crystal Structure of Tetrakisimidazole Cu(II) Sulphate, $Cu(C_3H_4N_2)_4SO_4$

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The crystal structure of $Cu(C_3H_4N_2)_4SO_4$ has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $C2/c$, with cell dimensions and corresponding standard deviations (at 25°C). $a = 9.224 \pm 0.001$ Å, $b = 17.626 \pm 0.001$ Å, $c = 10.552 \pm 0.001$ Å and $\beta = 93.473 \pm 0.004°$. There are four formula units per unit cell. The intensities were collected and measured using the linear diffractometer PAILRED with Mo$K\alpha$-radiation. With anisotropic thermal parameters the structure was refined to a conventional R-value = 0.050. The coordination around copper is a distorted octahedron and the ligand atoms are four imidazole nitrogens and two sulphate oxygens. $Cu(C_3H_4N_2)_4^{2+}$ ions are linked together by SO_4^{2-} ions, forming symmetry-related chains and these chains form layers parallel to the $a-c$ plane. The bond distances are Cu–N, 2.000 Å and 2.021 Å and Cu–O, 2.574 Å. Short interatomic contacts between sulphate oxygens and imidazole nitrogens conform to reasonable hydrogen-bond lengths (2.707, 3.020, 3.153 Å).

In continuation of the studies of metal-imidazole complexes in this department crystalline Cu(II)-imidazole complexes with sulphate as anion have been prepared. Since the coordination around copper is different when the anion is chloride [1] compared with perchlorate [2] we became interested in investigating crystalline Cu(II)-imidazole complexes with a bivalent anion such as SO_4^{2-}. So far two crystalline complexes containing sulphate have been obtained. One of these is a hydrate having the formula $Cu(C_3H_4N_2)_3SO_4.H_2O$ (under investigation) and the other is $Cu(C_3H_4N_2)_4SO_4$ which is the subject of the present publication.

EXPERIMENTAL

Crystal preparation. In a typical preparation of the crystals, 40 ml of a 1 M $C_3H_4N_2$ solution were added to 10 ml of a solution which was 1 M with respect to $CuSO_4$. The dark violet crystals in the shape of well defined rectangular prisms were obtained by slow evaporation of this solution at room-temperature.

Analysis. The copper content of the crystals was determined by titration with EDTA.[3] The found weight % was 14.3 compared with the calculated value 14.7. The content of N in $C_3H_4N_2$ was determined using the Kjeldahl method.[4] The found weight % was 25.7 compared with the calculated value 26.0. The absence of H_2O was confirmed with the aid of IR-spectra.[5] The sulphate was taken as the difference.

Unit cell data and space group. From rotation photographs around [100], [010], and [001] and the corresponding Weissenberg photographs (zero, first and second layer) taken with Cu$K\alpha$-radiation, it was concluded that the crystals are monoclinic. The cell dimensions and the angles were refined from a Guinier photograph using $Pb(NO_3)_2$ as an internal standard. The refinement was based on 90 lines, and the following parameters and their standard deviations were obtained: $a = 9.224 \pm 0.001$ Å; $b = 17.626 \pm 0.001$ Å; $c = 10.552 \pm 0.001$ Å; $\beta = 93.473 \pm 0.004°$ and $V = 1712.42$ Å^3. By the flotation method, using bromoform and xylene, the density of the crystals was determined to be 1.67 g/cm^3. With four formula units $Cu(C_3H_4N_2)_4SO_4$ in the unit cell the calculated density is 1.68 g/cm^3. Systematic extinctions for hkl when $h+k$ is odd and for $h0l$ when l is odd indicate the space group $C2/c$ or Cc.[6] The two space groups only differ in centrosymmetry.

The intensity material. 2026 independent reflections were collected and measured using an automatic linear diffractometer (PAILRED), with LiF-monochromator. The radiation used was Mo$K\alpha$. The integrated reflections were corrected for background in the usual way.[2] Reflections with a relative statistical error ($\Delta I/I$) greater than 0.5 were omitted and this reduction resulted in a remaining data set of 1459 observed reflections. There could be about 1850 independent reflections in the sphere of reflection for Cu$K\alpha$-radiation in this case. As a final check when the refinement was completed the structure factors of the omitted reflections were calculated. The check confirmed that all these omitted reflections had structure factors lower than or close to the threshold value.

The intensity material was first corrected for Lorentz and polarization factors but not for absorption. The crystal size was $0.024 \times 0.016 \times 0.012$ cm and the absorption correction was applied just before the refinement was fully completed. The linear absorption coefficient was calculated to be 14.80 cm^{-1}. The difference in the transmission factors were up to 9 % but there were negligible differences in the parameters when comparing the refinements before and after the absorption correction.

The computer programs used were the same as those reported earlier.[1]

STRUCTURE DETERMINATION AND REFINEMENT

The structure determination followed the usual routines of the heavy atom method with a three-dimensional Patterson synthesis and subsequent Fourier synthesis. There were no difficulties in finding the positions of the copper, sulphur, and oxygen atoms from the Patterson synthesis and the positions of the nitrogen and carbon atoms from the Fourier synthesis. However, to distinguish N2 from C2 and N4 from C5 all four atoms were refined as carbons and then the atoms with the lower temperature factors were labelled nitrogen. The positions of the nitrogens also seem to be in agreement with the hydrogen-bond distance to the sulphate oxygen atoms. By using the full-matrix-least-squares-method, the isotropic type of refinement of the various atomic parameters gave an R-value of 0.132. At this stage the intensity material was reduced for the ratio F_o/F_c within the limits $0.50 \leq F_o/F_c \leq 2.00$. The relative weighting factor used was that proposed by Cruickshank *et al.* $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ with $a = 30$, $c = 0.001$, and $d = 0$.

The refinement was then completed by introducing anisotropic temperature factors with the same restriction of the ratio F_o/F_c. This reduced the R to a final value of 0.050, and there were only 17 reflections outside the limits,

$0.50 \leq F_o/F_c \leq 2.00$. All of these reflections had low values of the structure factors.

Using the refined parameters a difference Fourier synthesis was calculated and the highest peak had a value of 0.66 $e^-/Å^3$. Some peaks occurring could be located to hydrogen positions but others not and no attempt was made to refine the hydrogen parameters. All parameter shifts in the final cycle were less than 10 % of the standard deviations. Atomic scattering factors for Cu^{2+}, S, O, N, and C were used,[7] where account was taken of the real part of the dispersion correction for Cu^{2+} and S. The final atomic coordinates and vibrational parameters are given in Table 1. A comparison between observed

Table 1. The atomic positional fractional coordinates, the anisotropic thermal parameters and their estimated standard deviations in parenthesis. 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	2500(0)	2500(0)	500(0)	96 (1)	20(0)	80(1)	9(1)	76 (1)	22(1)
S	0(0)	1396(1)	2500(0)	58 (2)	14(0)	79(1)	—	17 (2)	—
O1	550(6)	906(3)	1522(4)	258 (9)	69(2)	154(5)	172(7)	−118(11)	−117(6)
O2	1182(5)	1838(2)	3084(4)	218 (8)	51(2)	126(4)	−148(6)	− 5 (9)	−19(4)
N1	2835(4)	3344(2)	3784(3)	86 (5)	23(1)	72(3)	0(3)	36 (5)	10(3)
N2	3402(4)	4482(2)	3123(4)	124 (6)	24(1)	103(4)	−10(4)	45 (7)	28(3)
C1	3624(5)	3961(2)	4034(4)	103 (7)	27(1)	89(4)	−16(4)	23 (8)	18(4)
C2	2427(6)	4188(3)	2235(5)	159 (9)	28(2)	95(5)	9(5)	7(10)	22(4)
C3	2079(5)	3477(2)	2643(4)	117 (7)	27(1)	77(4)	4(4)	20 (7)	6(4)
N3	4314(4)	1956(2)	4515(3)	106 (5)	26(1)	74(3)	12(4)	52 (6)	9(3)
N4	6425(5)	1707(3)	3734(5)	98 (7)	52(2)	145(6)	40(6)	30 (9)	−11(6)
C4	5475(6)	2240(3)	4049(6)	87 (8)	43(2)	17(8)	7(6)	87(11)	− 3(7)
C5	5805(8)	1028(4)	4002(6)	185(11)	50(2)	116(6)	90(8)	97(12)	23(6)
C6	4511(7)	1182(3)	4481(6)	220(11)	51(2)	129(6)	59(7)	163(13)	21(5)

and calculated structure factors is given in Table 3. The reflections which are out of the range $0.50 \leq F_o/F_c \leq 2.00$ are marked with an asterisk. The acentric space group *Cc* was ruled out because the refinement in the centrosymmetric space group gave on the one hand somewhat better *R*-values and on the other more probable temperature factors for the oxygen and nitrogen atoms. Furthermore, refinement in the acentric space group gave very high correlation coefficients (of the order of ± 0.9) between the positional parameters of atoms which could be symmetry related. This was also a strong indication of centrosymmetry.[8]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The coordination around the copper atoms is a distorted octahedron with the two apical bonds to the oxygens in the sulfate groups a little longer than the four equatorial bonds to the nitrogens in the imidazole rings. The configuration around copper is shown in Fig. 1.

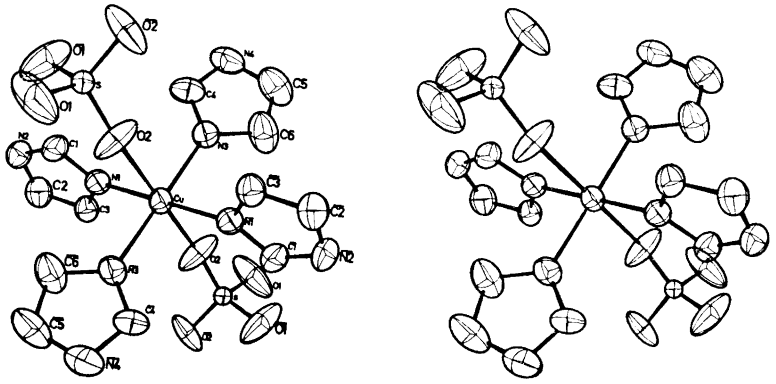

Fig. 1. Stereoscopic diagram (viewed along the negative direction of the c-axis) of the Cu-coordination. Thermal ellipsoids are scaled to enclose 50 % probability.

The arrangement of the imidazole rings around copper gives rise to $Cu(C_3H_4N_2)_4^{2+}$ ions which are linked together by SO_4^{2-} ions, forming symmetry related chains directed along the $a-c$ diagonal. The chains are held together through hydrogen bonds and van der Waals forces forming layers parallel to the $a-c$ plane. The layers repeat themselves for $y=\frac{1}{4}+N\times\frac{1}{2}$ ($N=$ integer).

The layers are held together with hydrogen bonds between the nitrogen N2 to the oxygen O1 and the nitrogen N2 in a symmetry related ring to another oxygen O1. These two distances are equal to 2.707(6) Å. The packing of the structure is shown in Fig. 2.

The coordination around copper. The copper atom is lying in the center of symmetry and the ligand atoms around Cu form a distorted octahedron. Four nitrogen atoms from the imidazole rings (N1, N3, and the symmetry related $\overline{N}1$ and $\overline{N}3$) laying at the corners of a rather distorted square have the shortest bond distances. The calculated Cu – N distances are 2.000(5) Å

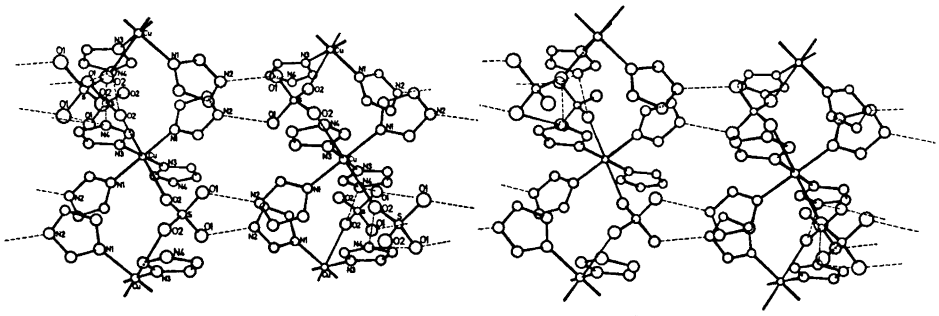

Fig. 2. Stereoscopic illustration of the molecular packing of $Cu(C_3H_4N_2)_4SO_4$ (viewed along the a-axis).

(Cu – N1) and 2.021(5) Å (Cu – N3). Because of the symmetry the Cu atom lies in the same plane as the four N atoms and the sides of the squares are 2.883(5) Å and 2.803(5) Å. The angle between the coordination directions N1 – Cu – N3 is 91.6(2)° and between N1 – Cu – $\bar{N}$3 it is 88.4(2)°. The oxygen atoms in the symmetry related sulphate groups lying on either side of the plane at a distance of 2.574(4) Å complete the distorted octahedron. The angles in the octahedron are O2 – Cu – N1 = 85.2(2)° and O2 – Cu – N3 = 86.9(2)°. In most structures with octahedral coordination around Cu(II) the octahedron is distorted due to the d^9 configuration of Cu(II). The distortion is generally explained by the Jahn-Teller theorem.[9] The average copper-nitrogen bond length (2.011 Å) is in good agreement with many other determinations.[2] The calculated copper-oxygen distance (2.574 Å) is a little longer than the copper-sulphate oxygen distance 2.41 Å in $CuSO_4.5H_2O$ [10] where the coordination around Cu(II) also forms an octahedron with two sulphate oxygens in the apical positions.

The imidazole rings. Two of the imidazole rings in the formula unit are unique and the other two are symmetry related. The interatomic distances and angles in the imidazole rings are listed in Table 2 and they are all within

Table 2. Bond lengths and bond angles in the imidazole rings. (Standard deviations for the last significant figure are shown in parentheses.)

	Bond length (Å)		Angle(°)
N1 – C1	1.326 (6)	C1 – N1 – C3	106.1(4)
N1 – C3	1.374 (6)	N1 – C1 – N2	111.2(4)
N2 – C1	1.337 (6)	C1 – N2 – C3	107.4(4)
N2 – C2	1.362 (7)	N2 – C2 – C3	106.8(5)
C2 – C3	1.370 (7)	C2 – C3 – N1	108.4(4)
N3 – C4	1.305 (7)	C4 – N3 – C6	104.9(5)
N3 – C6	1.377 (6)	N3 – C4 – N4	112.9(5)
N4 – C4	1.340 (8)	C4 – N4 – C6	106.0(5)
N4 – C5	1.365 (8)	N4 – C5 – C6	106.9(6)
C5 – C6	1.352(10)	C5 – C6 – N3	109.3(6)

the range of 1.305 Å – 1.377 Å and 104.9° – 112.9°. These interatomic distances and angles in the imidazole rings are about the same as found in other structure determinations.[2] Two planes based on the positions of the carbon and nitrogen atoms in the imidazole rings were calculated by a method discribed by Blow.[11] The equations for the planes are: 1st ring $0.7822x - 0.3879y - 0.4875z - 2.3691 = 0$, and 2nd ring $-0.3868x - 0.0324y - 0.9216z - 5.9172 = 0$. The maximum atomic positional deviations from the planes are for the first imidazole ring 0.004 Å and for the second imidazole ring 0.006 Å. The distance from the copper atom to the first plane is 0.354 Å and to the second plane 0.153 Å.

The sulphate group. In the sulphate group there are two unique and two symmetry related oxygen atoms. The arrangement around sulphur is a some-

Table 3. Observed and calculated structure factors (× 10).

K	L		
H=	0		
22	2	292	311
20	6	108	108
20	5	124	116
20	4	223	239
20	2	165	165
20	1	226	213
20	0	334	335
18	8	207	192
18	7	92	62
18	6	100	98
18	4	564	571
18	2	89	78
18	1	136	121
18	0	339	328
16	10	93	98
16	7	102	101
16	6	320	316
16	4	461	442
16	3	141	134
16	2	367	388
16	1	226	197
16	0	288	306
14	10	289	266
14	7	146	135
14	6	488	471
14	5	275	265
14	4	95	92
14	2	809	788
14	1	163	136
14	0	416	470
12	10	216	223
12	9	99	102
12	8	371	388
12	7	185	188
12	6	435	414
12	5	163	138
12	4	200	191
12	3	95	80
12	2	377	358
12	1	134	147
12	0	687	673
10	12	193	193
10	10	136	122
10	9	168	162
10	8	527	505
10	7	233	230
10	6	353	344
10	5	433	428
10	4	862	899
10	2	75	7*
10	1	234	254
10	0	571	603
8	12	242	242
8	10	149	134
8	8	565	581
8	7	161	158
8	5	180	178
8	4	808	799
8	3	543	546
8	2	1033	993
8	1	296	292
8	0	205	310
6	12	153	172
6	11	104	119
6	10	352	371
6	8	136	153
6	7	113	146
6	6	599	614
6	4	571	515
6	3	464	437
6	2	1259	1126
6	1	255	211
6	0	695	646
4	12	89	87
4	10	362	372
4	9	86	112
4	7	278	258
4	6	1065	1063
4	5	367	414
4	4	734	766
4	3	137	171
4	2	1445	1523
4	1	1090	1068
4	0	1240	1253
2	12	165	162
2	11	150	147
2	10	187	181
2	9	171	179
2	8	500	507
2	7	174	173
2	6	354	386
2	5	135	158
2	4	710	723
2	3	666	612
2	2	1355	1379
0	12	144	158
0	10	152	162
0	8	616	601
0	6	77	78
0	4	416	438
0	2	97	126
H=	1		
21	5	217	216
21	4	148	160
21	3	96	116
21	2	99	94
21	1	339	331
21	0	150	164
21	-1	149	157
21	-2	148	163
21	-3	150	170
21	-5	133	120
19	-6	122	126
19	-5	278	288
19	-4	110	124
19	-3	168	158
19	-2	292	273
19	-1	427	424
19	3	355	366
19	5	132	114
19	7	225	225
17	7	302	317
17	6	137	160
17	5	203	205
17	3	444	401
17	0	129	123
17	-1	521	505
17	-2	136	125
17	-3	305	305
17	-4	134	136
17	-5	293	293
17	-8	128	133
15	-8	187	182
15	-7	194	196
15	-5	274	276
15	-4	89	97
15	-3	337	327
15	-2	523	500
15	-1	271	277
15	0	151	127
15	1	697	696
15	2	96	68
15	3	186	186
15	4	189	185
15	5	493	528
15	6	273	290
15	7	108	140
15	9	179	189
13	10	114	100
13	9	284	284
13	5	390	397
13	4	118	126
13	3	325	340
13	1	710	675
13	0	178	140
13	-1	352	352
13	-2	118	139
13	-3	657	638
13	-4	132	172
13	-6	100	95
13	-7	610	595
13	-9	149	145
13	-10	140	137
13	-11	213	198
11	-10	169	166
11	-9	312	318
11	-7	395	413
11	-5	740	720
11	-4	75	46
11	-3	570	556
11	-2	242	235
11	-1	759	740
11	0	111	126
11	1	415	446
11	2	167	170
11	3	212	230
11	4	585	580
11	5	146	148
11	6	446	440
11	7	329	335
11	8	229	219
11	9	235	245
11	11	162	174
11	12	85	77
9	11	180	175
9	10	86	84
9	9	166	162
9	8	201	220
9	7	578	611
9	6	69	41
9	5	70	88
9	4	171	147
9	3	503	557
9	2	231	180
9	1	522	517
9	0	371	372
9	-1	806	852
9	-2	300	268
9	-3	374	378
9	-5	1085	1098
9	-7	115	101
9	-9	516	516
9	-10	155	149
7	-11	173	184
7	-10	88	67
7	-9	426	445
7	-8	159	156
7	-7	578	560
7	-6	362	355
7	-5	168	185
7	-4	284	309
7	-3	1046	1088
7	-2	230	171
7	-1	579	554
7	0	253	237
7	1	665	534
7	2	198	151
7	3	1246	1240
7	4	228	217
7	5	447	450
7	6	474	479
7	7	361	388
7	8	253	263
7	9	81	74
7	10	305	291
7	11	236	229
7	13	186	158
5	13	140	151
5	11	153	178
5	10	75	51
5	9	216	212
5	7	306	312
5	6	203	200
5	5	971	950
5	4	229	254
5	3	234	187
5	1	1340	1297
5	0	584	608
5	-1	138	168
5	-2	260	283
5	-3	1550	1578
5	-5	453	412
5	-7	753	766
5	-8	161	156
5	-9	143	125
5	-10	179	200
5	-11	369	390
3	-13	182	146
3	-12	81	55
3	-11	238	238
3	-10	166	161
3	-9	136	149
3	-8	77	57
3	-7	598	590
3	-6	644	628
3	-5	803	842
3	-4	475	522
3	-3	1101	1131
3	-2	387	443
3	-1	684	648
3	0	317	298
3	1	1097	1112
3	2	1456	1477
3	3	554	619
3	5	741	771
3	6	506	465
3	7	407	413
3	8	356	357
3	9	526	535
3	10	191	180
3	12	152	133
3	13	123	126
1	11	278	274
1	9	193	200
1	8	138	129
1	7	420	410
1	6	475	463
1	5	958	953
1	4	122	97
1	3	2317	2321
1	2	1857	1890
1	-2	154	156
1	-3	883	883
1	-5	756	794
1	-6	176	181
1	-7	323	342
1	-9	480	473
1	-11	101	87
1	-12	129	144
H=	2		
22	0	279	285
22	-3	96	98
22	-4	171	177
20	-6	160	168
20	-5	136	124
20	-4	154	181
20	-3	161	172
20	-2	119	137
20	-1	105	90
20	0	179	181
20	1	163	155
20	2	283	306
20	3	207	216
20	4	162	157
20	6	181	172
18	6	210	241
18	5	81	96
18	4	213	202
18	2	367	361
18	-1	124	111
18	-2	465	454
18	-4	140	104
18	-6	257	260
16	-10	162	155
16	-9	139	136
16	-8	196	185
16	-6	236	243
16	-5	310	306
16	-4	129	144
16	-3	170	163
16	-2	367	371
16	-1	91	56
16	0	205	196
16	1	429	424
16	2	359	343
16	3	389	396
16	4	216	232
16	5	218	254
16	6	320	325
16	8	131	136
16	9	138	147
14	8	248	258
14	7	183	185
14	6	171	150
14	4	490	488
14	3	137	141
14	2	273	287
14	1	91	90
14	0	650	627
14	-1	208	229
14	-2	209	210
14	-3	155	158
14	-4	326	320
14	-5	374	378
14	-6	273	267
14	-7	198	207
14	-8	343	348
14	-10	119	100
12	-11	136	162
12	-8	422	428
12	-7	247	249
12	-6	234	217
12	-5	208	202
12	-4	582	600
12	-3	352	326
12	-2	530	548
12	-1	363	353
12	0	1011	1009
12	1	314	280
12	2	301	249
12	3	539	526
12	4	560	576
12	5	98	92
12	7	291	281
12	8	306	299
12	9	154	142
12	10	96	89
10	11	121	110
10	10	133	149
10	8	128	122
10	6	489	494
10	5	248	223
10	4	78	48
10	3	240	239
10	2	713	698
10	0	1036	973
10	-1	164	150
10	-2	917	890
10	-3	197	160
10	-4	544	569
10	-5	90	110
10	-6	564	528
10	-7	127	131
10	-8	223	244
10	-10	275	282
8	-12	114	111
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Table 1. Continued.

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11	11	140	126	1	-2	202	206	10	0	104	120	2	9	80	107	9	3	145	153	1	6	234	240	8	1	364	353
9	11	144	144	1	-3	725	685	10	2	579	568	2	10	111	125	9	2	192	212	1	5	386	378	8	0	394	380
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5	-1	98	95	14	8	174	168	6	9	121	118	15	5	145	156	5	-2	196	203	14	6	150	164	4	-7	139	152
5	-2	258	254	14	7	93	73	6	10	77	33*	15	7	108	111	5	-3	293	288	12	10	84	76	4	-8	192	193
5	-3	1226	1275	14	4	252	242	4	12	98	101	15	8	147	122	5	-4	173	186	12	9	80	73	4-10		230	240
5	-4	136	113	14	3	73	33*	4	8	184	200	13	7	199	201	5	-5	377	376	12	8	134	130	2-13		108	83
5	-5	218	201	14	2	177	186	4	7	199	192	13	6	87	66	5	-6	158	142	12	5	104	101	2-12		143	136
5	-6	112	98	14	0	442	430	4	6	120	130	13	3	229	236	5	-7	307	284	12	4	88	69	2-11		206	208
5	-7	609	633	14	-1	198	204	4	4	556	566	13	2	253	239	5	-8	164	152	12	2	327	335	2	-9	111	127
5	-8	213	210	14	-2	86	89	4	2	70	64	13	1	170	153	5	-9	299	308	12	1	183	189	2	-8	308	314
5	-9	170	157	14	-4	420	414	4	1	123	130	13	-1	367	389	5-11		134	130	12	0	232	220	2	-7	154	108
5-11		401	370	14	-6	104	89	4	0	670	660	13	-2	129	126	5-13		168	156	12	-1	178	158	2	-6	448	446
3-13		98	73	14	-8	272	280	4	-1	245	268	13	-3	134	134	3-13		134	138	12	-2	166	189	2	-5	126	123
3-11		258	271	12-11		105	84	4	-2	577	560	13	-4	217	222	3-12		88	96	12	-3	112	92	2	-4	349	332
3-10		146	134	12-10		98	122	4	-3	76	55	13	-5	410	405	3-11		151	145	12	-4	228	222	2	-3	401	382
3	-9	335	341	12	-8	285	293	4	-4	811	814	13	-7	81	90	3-10		119	131	12	-5	208	221	2	1	167	164
3	-8	88	97	12	-7	182	180	4	-5	370	344	13	-9	242	236	3	-9	370	367	12	-6	256	267	2	2	358	359
3	-7	607	619	12	-6	379	378	4	-6	198	190	11	-9	149	136	3	-8	79	31*	12	-7	116	119	2	3	248	271
3	-6	259	271	12	-4	544	528	4	-8	501	515	11	-8	195	165	3	-7	133	141	12	-8	95	89	2	4	217	229
3	-5	509	540	12	-3	76	63	4-10		144	139	11	-7	351	353	3	-6	250	287	12	-9	147	131	2	5	92	76
3	-4	392	354	12	-1	408	422	4-12		247	231	11	-6	85	78	3	-5	504	502	12-10		118	121	2	6	144	139
3	-3	412	416	12	0	416	410	2-12		111	118	11	-5	347	356	3	-4	417	416	10	-9	134	127	2	8	121	117
3	-2	99	71	12	1	82	67	2-10		247	240	11	-4	158	143	3	-3	196	225	10	-8	302	275	0	10	100	90
3	-1	555	569	12	2	261	268	2	-9	243	268	11	-3	351	343	3	-2	223	191	10	-6	242	253	0	8	202	222
3	0	253	250	12	3	96	61	2	-8	185	153	11	-2	275	283	3	-1	483	500	10	-4	274	283	0	6	98	89
3	1	1156	1147	12	4	200	204	2	-7	102	135	11	-1	297	290	3	0	704	702	10	-3	220	228	0	4	433	449
3	2	88	91	12	5	207	194	2	-6	478	528	11	0	199	199	3	1	586	550	10	-2	175	174	0	-2	80	49
3	4	286	264	12	7	111	115	2	-5	87	51	11	1	334	317	3	2	149	168	10	0	436	417	0	-4	459	432
3	5	580	580	12	8	174	166	2	-4	524	537	11	2	260	241	3	3	408	391	10	2	213	206	0	-6	401	398
3	6	186	181	12	10	84	63	2	-3	355	359	11	3	258	263	3	4	423	423	10	4	273	271	0	-8	397	427
3	7	75	65	10-10		287	271	2	-2	529	525	11	7	80	93	3	5	185	207	10	5	147	151	0-10		123	113
3	8	208	234	10	-8	313	324	2	2	639	644	11	8	108	107	3	6	258	246	10	7	71	58	0-12		257	243
3	9	203	194	10	-6	555	572	2	3	548	527	11	10	82	79	3	7	102	141	10	8	106	107				
1	11	110	121	10	-5	194	201	2	4	295	305	9	9	159	162	3	10	164	97	8	8	131	147				

what distorted tetrahedron. The sulphur-oxygen distances are S–O1 = 1.460(5) Å and S–O2 = 1.448(5) Å and the angles are O1–S–O2 = 109.6(3)°; O1–S–$\bar{O}$2 = 107.6(3)°C; O1–S–$\bar{O}$1 = 107.5(4)° and O2–S–$\bar{O}$2 = 114.8(4)°.

The interatomic distances and angles in the sulphate group are in good agreement with those in a recent tabulation [12] except for the angle O2–S–$\bar{O}$2 which differs from the tetrahedral angle by 5.3°. This difference is probably due to the coordination of O2 and $\bar{O}$2 to the copper atoms.

Hydrogen bonds. The interatomic distances in the layers between the nitrogen N4 and the oxygen O1 and between the same nitrogen N4 and the oxygen O2 are 3.153(7) Å and 3.020(6) Å, respectively. These distances indicate a bifurcated hydrogen bond holding the chains together. Between the layers the earlier mentioned hydrogen bonds (N2–H···O1) are stronger and have the distance 2.707(6) Å. These hydrogen bonds can cause the imidazole rings involved to bend towards the oxygen atoms and owing to that the copper

atom lies further out of the plane defined by the atoms in the mentioned imidazole ring than from the other plane. The hydrogen bond distances are all within the range given by International Tables.[7]

Acknowledgements. The authors thank Professor Nils Ingri for his interest and for the facilities placed at our disposal. This work forms part of a program supported by *Statens Naturvetenskapliga Forksningsråd.*

REFERENCES

1. Lundberg, B. K. S. *Acta Chem. Scand.* **26** (1972) 3902.
2. Ivarsson, G., Lundberg, B. K. S. and Ingri, N. *Acta Chem. Scand.* **26** (1972) 3005.
3. Kolthoff, I. M., Sandell, E. B., Meehan, E. J. and Bruckenstein, S. *Quantitative Chemical Analysis*, 4th Ed., Macmillan, London 1969, pp. 744 – 747.
4. Kjelldahl, J. *Z. anal. Chem.* **22** (1883) 366.
5. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Methuen, London 1964.
6. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1965, Vol. I.
7. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
8. Stout, G. H. and Jensen, L. H. *X-Ray Structure Determination. A Practical Guide*, Macmillan, London 1968.
9. Orgel, L. E. *An Introduction to Transition-Metal Chemistry Ligand-Field Theory*, Methuen, London 1960, pp. 57 – 65.
10. Bacon, G. E. and Curry, N. A. *Proc. Roy. Soc. (London)* **A 266** (1962) 95.
11. Blow, D. M. *Acta Cryst.* **13** (1960) 168.
12. Andreetti, G. A., Cavalca, L. and Musatti, A. *Acta Cryst.* **B 24** (1968) 683.

Received May 3, 1972.