ACTA CHEMICA SCANDINAVICA 26 (1972) 3977–3983

Metal Complexes with Mixed Ligands

5. The Crystal Structure of Diimidazole-copper(II) Dichloride, $Cu(C_3H_4N_2)_2Cl_2$

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The crystal structure of diimidazole-copper(II) dichloride has been determined using three-dimensional X-ray diffraction data. The crystals belong to the orthorhombic space group $Pbn2_1$ (No. 33). The unit cell contains four formula units and has the dimensions $a = 12.969 \pm 0.001$ Å, $b = 10.796 \pm 0.001$ Å and $c = 6.803 \pm 0.001$ Å. The copper atom coordinates five ligand atoms in a tetragonal pyramidal configuration. The four closest ligand atoms lying at the corners of an approximately square plane are two nitrogen atoms (with the distances Cu – N = 1.97 Å and 1.99 Å) and two chlorine atoms (with the distances Cu – Cl = 2.32 Å and 2.37 Å). The apex of the pyramid is a chlorine atom at the distance Cu – Cl = 2.75 Å. This chlorine atom lies in the coordination plane of another pyramid too. Since only one chlorine atom forms a bridge between successive symmetry related copper atoms a polynuclear chain with alternating short and long Cu – Cl distances is formed. The chains are held together by hydrogen bonds between adjacent chains. The distances N – H···Cl are 3.16 Å and 3.39 Å.

The investigation of the crystal structure of $Cu(C_3H_4N_2)_2Cl_2$ was undertaken as part of a research programme at this institute on metal imidazole complexes.[1–6] Copper-imidazole complexes with different ratios imidazole to copper have been crystallized from chloride medium. $Cu(C_3H_4N_2)_4Cl_2$ (under study) which has a deep blue colour is obtained at a ratio $C_3H_4N_2$:Cu of about 10:1 and pH about 8.0. At the same ratio but a slightly lower pH (7.5 – 8.0) the light blue crystals of $Cu(C_3H_3N_2)(C_3H_4N_2)_2Cl$ are formed.[1] When the ratio of imidazole to copper is about 2:1 and at pH about 5.0 it is possible to obtain green crystals of $Cu(C_3H_4N_2)_2Cl_2$, by almost complete evaporation of the solution. This complex is the subject of this communication.

EXPERIMENTAL

Crystal preparation and analyses. In a typical preparation 0.7 ml of a 1 M $CuCl_2$ solution were added to 1.4 ml of a 1 M $C_3H_4N_2$ solution and the pH of the mixture was

adjusted to about 5.0 by adding 0.1 M hydrochloric acid. The solution was left at room temperature for slow evaporation and when this was almost completed green crystals in the shape of thin plates were formed.

The copper content was determined electrolytically, the chlorine content by titration with silver nitrate and the nitrogen content was determined using the Kjeldahl method. (Found: Cu 22.9; Cl 26.1; N 20.5. Calc. for $Cu(C_3H_4N_2)_2Cl_2$: Cu 23.5; Cl 26.2; N 20.7.) The density of the crystals was determined by the flotation method to be 1.89 g/cm³. The calculated density with four formula units in the cell is 1.89 g/cm³.

Crystal data and space group. From rotation photographs and corresponding Weissenberg equi-inclination photographs ($h0l - h2l$ and $hk0 - hk2$) taken with Cu$K\alpha$-radiation it was concluded that the crystals are orthorhombic. The systematic extinctions found were for $h0l$, $h+l=2n+1$ and for $0kl$, $k=2n$ which is characteristic for the space groups *Pbnm* (No. 62) and $Pbn2_1$ (No. 33).[7]

The cell dimensions were calculated and refined from a powder photograph taken with a focusing camera of Guinier-Hägg type. The following parameters and their corresponding standard deviations were obtained: $a=12.969\pm0.001$ Å, $b=10.796\pm0.001$ Å and $c=6.803\pm0.001$ Å.

Collection and reduction of intensity data. The intensities were collected using an automatic linear diffractometer (PAILRED), with Mo$K\alpha$-radiation and a LiF monochromator. The crystal that was rotated around the c axis had the dimensions $0.004\times0.010\times0.020$ cm in the crystallographic a, b, and c directions. The intensities at about 2600 lattice points in the layers $\pm hk0 - \pm hk6$ were measured. Those reflections which had a negative net count and those which were not significant at the 95 % level,[8] *i.e.* had $\Delta I/I > 0.50$, were omitted which left 1241 observed intensities. After the usual Lorentz-polarization and absorption corrections the mean values for identical observed structure factors ($F(hkl)$ and $F(\bar{h}kl)$) were calculated. This resulted in 729 independent reflections.

Computer programs used. The diffractometer data correction was made with a program written at this department (Ivarsson, Lundberg). The computer programs for Lorentz and polarization corrections, Fourier summations and for the calculation of distances and angles were originally written by A. Zalkin. A modified version of a program written by Gantzel, Sparks and Trueblood was used for structure factor calculation and refinement of the structural parameters. Correction for absorption was performed with a program originally written by P. Coppens, L. Leiserowitz and D. Rabinovich, revised by Olle Olofsson and Mats Elfström. The computer program ORTEP [9] was used to produce the stereoscopic figures. The computers used were CD 3600 and CD 3200.

STRUCTURE DETERMINATION

From the experimental data it was found that there are four formula units in the unit cell. When attempts were made to solve a three-dimensional Patterson synthesis assuming the atoms to be distributed according to positions in the centrosymmetric space group *Pbnm* it was found that the Cl atoms could not be situated in the general eightfold position. Neither could two chlorine atoms be situated in a fourfold special position each, according to the Patterson peaks assumed to have resulted from Cu – Cl vectors (length 2.39 Å). Thus the structure was solved using the general fourfold positions of the acentric space group $Pbn2_1$. All the Patterson peaks for Cu – Cl and Cu – N vectors were explained. Normal Fourier techniques gave the approximate positions of the other atoms.

STRUCTURE REFINEMENT

The refinement was made with full matrix least squares technique. The atomic scattering factors for carbon, nitrogen, chloride (Cl^-), and copper

(Cu^{2+}) were taken from *International Tables* [7] and account was taken of the real part of the dispersion correction for the copper and chlorine atoms. To identify the nitrogen atoms of the imidazole rings which are not coordinated to the copper atom the two possible atoms of each ring were both labelled nitrogen. Then the isotropic temperature factors which were higher should distinguish the carbon atoms. In one of the two cases the values were close to each other and the standard deviation relatively high but the right choice could be made on the basis of possible hydrogen bond lengths to chlorine atoms.

A completed refinement using isotropic temperature factors gave an *R*-value of 0.080. When converting to the anisotropic type of refinement the temperature factors for a few atoms in the imidazole rings were not positive definite. This is probably due to the fact that all the heavy atoms (Cu, Cl1, and Cl2) lie close to the mirror glide plane and that the positions for the atoms of the imidazole ring on one side of this plane are strongly correlated to the atomic positions of the imidazole ring on the other side. As a result of this most of the reflections when $h+k=2n+1$ have low values. Regarding this the refinement was completed with anisotropic thermal parameters for only Cu, Cl 1, and Cl 2, giving an *R*-value of 0.069. Several weighting schemes were applied and the one recommended by Hughes [10] which gave the best weight analysis, was used in the last refinement. Although some of the calculated standard deviations for the bond distances found are higher than in similar structures [1,5] the bond distances and angles have values in the expected ranges showing a satisfactory refinement.

All parameter shifts in the last cycle were less than 10 % of the corresponding standard deviations and a final difference Fourier synthesis showed no anomalies. Although some peaks in this difference Fourier synthesis could originate from hydrogen atoms there were other equally high peaks in impossible positions. Therefore no attempts were made to include hydrogen

Table 1. The atomic positional fractional coordinates ($\times 10^4$) and thermal parameters. Anisotropic temperature factors have been calculated for the first three atoms according to the formula $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$ and the values for β_{ij} are multiplied by 10^4. The standard deviations for the last significant figure are shown in parentheses.

	x	y	z	β_{11} *el.*β	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	15 (2)	1269 (2)	0	19 (1)	29(1)	55 (4)	1(2)	60 (6)	16 (6)
Cl1	106 (4)	3411 (4)	−237(17)	23 (2)	35(3)	361(22)	1(4)	65(18)	25(17)
Cl2	−63 (4)	−824 (4)	1019 (9)	30 (2)	44(3)	101(12)	−15(6)	−43(13)	29(10)
N1	1532 (9)	1197(13)	208(32)	1.18(24)					
N2	3101(11)	388(15)	−139(44)	2.39(27)					
C1	2082(10)	187(12)	−503(25)	1.15(21)					
C2	3186(17)	1537(23)	740(42)	2.73(39)					
C3	2243(14)	2030(17)	920(40)	1.61(31)					
N3	−1517(10)	1396(14)	69(41)	1.63(25)					
N4	−3092(12)	1959(16)	831(32)	1.83(27)					
C4	−2081(17)	2273(23)	956(48)	2.74(40)					
C5	−3163(11)	833(15)	−99(53)	1.48(24)					
C6	−2195(12)	515(15)	−430(33)	1.13(27)					

Table 2. Observed and calculated structure factors (× 10). Those marked with an asterisk were not included in the refinement ($F_o/F_c > 4.0$).

K	H			K	H			K	H			K	H			K	H			K	H			K	H		
				1	13	572	546	5	5	831	832	8	3	144	122	10	6	379	396	11	7	314	328	7	9	248	237
L=	0			1	12	175	219	5	3	926	949	8	2	528	526	10	4	351	335	11	5	317	299	7	7	277	319
				1	11	186	160	5	1	1248	1229	8	0	518	536	10	2	360	369	11	3	271	286	7	5	235	291
16	3	130	55	1	10	204	218	4	15	146	102	7	16	136	89	10	0	524	493	11	1	365	362	7	3	305	311
15	7	265	239	1	9	683	690	4	14	121	100	7	15	174	147	9	13	241	224	10	8	173	147	7	1	345	342
15	6	133	142	1	8	171	197	4	13	116	142	7	13	145	139	9	11	212	231	10	7	165	139	6	14	278	293
15	5	218	239	1	7	711	682	4	10	187	198	7	11	176	188	9	9	212	228	10	4	212	216	6	12	237	273
15	3	235	226	1	6	270	258	4	9	119	165	7	9	193	165	9	7	368	367	10	1	139	122	6	10	233	252
15	1	293	284	1	5	778	713	4	8	119	118	7	8	125	113	9	5	386	378	10	0	270	266	6	8	363	367
14	6	130	112	1	4	160	156	4	6	198	230	7	7	289	280	9	3	258	279	9	9	223	190	6	6	435	425
14	4	160	104	1	3	878	840	4	4	314	334	7	5	330	331	9	1	453	446	9	7	361	354	6	4	366	383
13	11	141	87	1	2	116	105	4	1	148	145	7	4	135	159	8	13	143	164	9	5	301	300	6	2	361	358
13	9	129	125	0	20	291	270	4	0	574	606	7	3	186	117	8	12	274	257	9	3	343	345	6	0	615	606
13	7	171	178	0	18	316	335	3	15	123	131	7	1	364	372	8	10	139	130	9	1	387	381	5	13	179	173
13	5	184	172	0	16	434	384	3	14	131	82	6	14	193	198	8	8	226	256	8	12	325	317	5	11	271	275
13	3	146	158	0	14	701	767	3	13	291	291	6	12	171	138	8	6	278	303	8	10	280	290	5	9	170	176
13	1	206	206	0	12	723	696	3	11	130	103	6	10	221	240	8	4	179	206	8	8	427	434	5	7	271	320
12	14	139	126	0	10	1226	1186	3	10	107	111	6	8	282	305	8	2	434	464	8	6	479	506	5	5	425	430
12	8	112	70	0	8	893	898	3	9	316	313	6	6	299	300	8	0	132	151	8	4	437	440	5	3	203	172
12	1	133	132	0	6	2031	2151	3	8	176	156	6	4	386	398	7	13	161	183	8	2	490	503	5	1	456	461
11	13	154	135	0	4	1761	2113	3	7	445	440	6	2	429	419	7	12	193	158	8	0	619	614	4	10	248	269
11	12	136	166	0	2	692	772	3	5	356	349	6	0	374	411	7	11	188	194	7	13	264	267	4	9	192	169
11	9	118	109					3	4	151	148	5	15	242	232	7	9	144	128	7	11	254	262	4	6	302	272
11	7	141	139	L=	1			3	3	403	389	5	13	326	330	7	8	187	229	7	10	140	76	4	4	359	321
11	5	193	209					3	1	477	483	5	11	382	391	7	7	307	337	7	9	284	286	4	1	183	169
11	4	193	217	15	3	134	113	2	16	141	129	5	10	148	190	7	5	221	240	7	7	373	388	4	0	599	565
11	1	209	223	15	1	152	145	2	16	128	103	5	9	349	331	7	4	168	191	7	5	497	490	3	13	412	425
10	6	148	137	14	6	384	374	2	14	185	210	5	7	682	679	7	3	277	288	7	4	178	178	3	11	283	262
10	2	150	153	14	4	390	393	2	13	153	148	5	6	202	196	7	1	302	317	7	3	276	268	3	9	475	509
10	0	180	157	14	2	406	418	2	12	241	214	5	5	567	565	6	16	170	171	7	2	120	108	3	7	542	550
9	15	207	210	14	0	469	468	2	10	237	222	5	3	667	589	6	15	164	164*	7	1	544	533	3	5	568	559
9	13	237	231	13	9	168	161	2	9	240	259	5	1	813	747	6	14	241	274	6	12	162	150	3	3	579	606
9	11	315	317	13	7	218	224	2	8	191	156	4	16	248	276	6	12	343	374	6	10	247	233	3	2	138	90
9	9	334	316	13	6	121	82	2	8	637	647	4	14	355	372	6	10	208	207	6	9	137	104	3	1	688	677
9	7	420	413	13	5	208	217	2	5	198	219	4	13	198	93	6	8	474	481	6	8	359	343	2	15	179	31*
9	5	562	563	13	3	167	155	2	4	207	183	4	12	635	620	6	6	548	548	6	7	139	139	2	14	335	370
9	4	147	213	13	1	242	254	2	3	149	144	4	10	426	420	6	4	345	360	6	6	284	294	2	12	454	468
9	3	395	354	11	9	122	124	2	2	687	717	4	8	774	792	6	2	609	590	6	4	369	382	2	10	331	395
9	2	151	164	11	7	138	114	2	1	247	251	4	7	187	146	6	0	574	580	6	2	438	437	2	8	542	566
9	1	626	605	11	5	178	187	2	0	1413	1366	4	6	1082	1040	5	15	246	220	6	0	396	384	2	6	788	756
8	15	210	219	11	4	154	206	1	17	152	117	4	4	712	724	5	13	236	294	5	13	229	222	2	4	525	551
8	14	259	255	11	1	159	184	1	15	237	218	4	3	122	105	5	11	389	398	5	12	181	157	2	2	706	709
8	13	123	128	10	14	169	184	1	13	512	516	4	2	1164	1144	5	9	313	301	5	11	144	111	2	0	876	857
8	12	266	260	10	12	306	315	1	11	263	247	4	0	1250	1247	5	8	159	149	5	10	133	152	1	15	229	250
8	10	143	152	10	10	415	413	1	10	146	122	3	17	140	125	5	7	610	620	5	9	199	194	1	14	181	175
8	9	338	353	10	8	506	513	1	9	627	632	3	15	162	120	5	6	118	78	5	8	149	117	1	13	297	310
8	8	379	374	10	7	165	179	1	8	105	104	3	13	261	291	5	5	611	609	5	7	274	293	1	12	162	105
8	6	428	426	10	6	613	620	1	7	741	748	3	12	128	124	5	3	441	444	5	6	168	149	1	11	404	403
8	4	237	234	10	4	622	619	1	6	158	128	3	11	213	186	5	1	798	777	5	5	248	251	1	9	303	330
8	3	192	170	10	2	594	588	1	5	763	760	3	10	145	152	4	15	162	137	5	3	207	209	1	7	639	643
8	2	491	467	10	1	38	38	1	3	867	852	3	9	194	234	4	14	181	179	5	1	382	415	1	5	517	549
8	1	115	142	10	0	834	845	0	17	151	105	3	8	166	177	4	13	147	142	4	14	284	304	1	3	527	548
8	0	379	394	9	15	265	283	0	13	140	126	3	7	445	460	4	10	380	389	4	12	375	366	0	11	235	218
7	11	117	111	9	14	137	146	0	9	140	155	3	6	130	98	4	9	212	208	4	10	283	296	0	7	187	208
7	9	117	100	9	13	316	305	0	7	149	170	3	5	190	222	4	8	158	133	4	9	126	99				
7	7	169	180	9	11	370	390	0	3	116	83	3	3	192	202	4	6	393	403	4	8	473	488	L=	6		
7	3	153	133	9	10	122	141					3	1	422	390	4	4	574	555	4	6	661	641				
7	2	126	83	9	9	411	411	L=	2			2	12	222	217	4	3	159	132	4	4	484	489	11	5	228	234
7	1	103	114	9	8	108	115					2	9	155	196	4	1	170	243	4	2	556	569	11	1	262	288
5	19	157	156	9	7	538	558	15	3	170	186	2	8	316	321	4	0	990	958	4	0	862	843	10	8	218	83
5	18	134	78	9	6	129	169	15	1	229	249	2	7	139	144	3	17	176	127	3	15	189	180	10	3	161	83
5	17	220	219	9	5	658	679	14	0	163	133	2	6	172	171	3	16	152	144	3	13	225	241	10	0	187	175
5	15	304	289	9	3	519	489	13	9	209	194	2	4	124	54	3	15	244	228	3	11	279	284	9	7	229	225
5	13	401	392	9	2	134	176	13	8	154	44	2	2	866	817	3	13	411	442	3	9	222	233	9	5	224	172
5	12	119	89	9	1	751	765	13	7	222	233	2	1	137	142	3	11	230	234	3	7	411	421	9	3	194	214
5	11	508	521	8	12	133	130	13	5	245	275	2	0	498	335	3	10	145	170	3	5	374	367	9	1	214	219
5	10	169	189	8	11	122	99	13	3	234	245	1	15	192	216	3	9	571	589	3	3	182	196	7	8	195	68
5	9	443	414	8	10	107	75	13	1	277	302	1	14	134	162	3	7	594	585	3	1	501	476	7	6	194	75
5	7	947	921	8	8	128	135	12	8	202	174	1	13	444	458	3	6	164	144	2	13	147	180	6	9	201	123
5	6	206	208	8	6	168	165	12	6	183	181	1	11	194	202	3	5	706	678	2	12	238	225	6	7	168	144
5	5	760	732	8	4	105	111	12	4	161	162	1	10	146	176	3	3	682	696	2	11	155	135	5	9	217	188
5	3	858	861	8	2	223	246	12	2	189	164	1	9	494	507	3	1	439	431	2	8	332	334	5	7	188	193
5	1	1158	1079	8	0	108	104	12	1	119	122	1	8	157	152	2	16	149	205	2	2	664	641	5	5	228	159
4	19	119	24*	7	15	137	81	12	0	273	256	1	7	622	624	2	15	137	47	2	1	121	127	5	3	245	258
4	18	273	254	7	13	119	68	11	9	201	184	1	6	177	194	2	14	301	334	2	0	319	283	5	1	192	203
4	17	198	200	7	11	171	166	11	7	218	250	1	5	494	499	2	12	347	396	1	15	157	113	4	11	173	94
4	16	346	342	7	10	105	108	11	5	273	269	1	4	146	99	2	10	351	375	1	13	264	257	4	10	243	247
4	15	137	144	7	9	116	49	11	4	148	142	1	3	759	725	2	8	470	467	1	10	135	100	4	8	308	341
4	14	407	408	7	7	208	232	11	3	228	212	0	18	234	249	2	6	848	819	1	9	168	161	4	6	417	409
4	13	149	160	7	5	133	145	11	1	299	311	0	16	317	312	2	4	519	521	1	7	387	393	4	4	351	363
4	12	806	762	7	4	106	134	10	12	141	86	0	14	508	552	2	2	540	542	1	5	155	136	4	3	186	94
4	11	211	222	7	3	130	121	10	10	144	115	0	12	596	582	2	0	1271	1200	1	3	324	294	4	2	365	381
4	10	522	490	7	2	104	111	10	8	143	151	0	10	863	845	1	17	183	175	1	2	110	54	4	0	604	562
4	9	126	117	7	1	212	212	10	6	149	161	0	8	708	714	1	15	264	276	0	14	233	282	3	11	300	265
4	8	993	970	6	17	155	142	10	5	113	39	0	6	1533	1493	1	13	421	434	0	12	400	375	3	9	211	170
4	7	279	303	6	16	181	188	10	4	196	204	0	4	1242	1345	1	11	421	443	0	10	278	315	3	7	353	301
4	6	1355	1338	6	15	134	146	10	3	122	41	0	2	674	693	1	9	512	499	0	8	438	416	3	5	373	373
4	4	889	864	6	14	241	235	10	2	146	148					1	7	838	821	0	6	754	754	3	3	205	126
4	3	139	183	6	13	164	159	10	0	271	270	L=	3			1	5	735	752	0	4	402	423	3	1	429	399
4	2	1644	1569	6	12	473	475	9	14	130	60					1	3	821	814	0	2	540	533	2	10	179	87
4	0	1449	1514	6	11	257	285	9	13	230	209	14	6	259	254	0	17	183	188					2	8	170	167
3	19	186	114	6	10	136	137	9	11	285	300	14	5	139	69	0	15	182	191	L=	5			2	2	257	245
3	16	137	143	6	8	575	596	9	10	126	130	14	4	236	241	0	13	158	186					2	0	187	182
3	13	283	292	6	7	187	240	9	9	254	274	14	2	285	280	0	11	274	277	13	2	172	64	1	7	275	266
3	12	154	168	6	6	680	657	9	7	421	418	14	0	325	305	0	9	146	202	13	1	188	159	1	5	232	180
3	11	115	89	6	5	191	196	9	5	467	475	13	7	225	194	0	7	282	263	10	9	160	44	1	3	207	195
3	10	127	89	6	4	256	279	9	4	148	193	13	5	211	191	0	5	165	147	10	8	183	196	0	12	233	299
3	9	154	135	6	2	908	923	9	3	404	389	13	2	138	91					10	6	253	235	0	10	302	304
3	8	216	234	6	1	214	236	9	2	123	132	13	1	188	218	L=	4			10	4	165	175	0	8	368	339
3	7	484	451	6	0	437	426	9	1	529	541	12	10	143	69					10	2	186	219	0	6	458	458
3	4	176	156	5	17	211	230	8	15	170	164	12	5	149	125	13	3	275	256	10	0	238	249	0	4	385	401
3	3	189	120	5	15	311	298	8	14	291	276	11	5	129	120	13	1	293	316	9	7	186	182	0	2	460	463
3	1	261	242	5	13	424	437	8	12	278	292	11	4	128	103	12	6	271	306	9	5	206	160				
3	10	281	309	5	11	562	569	8	10	216	235	11	1	149	144	12	4	269	256	9	1	220	190				
3	18	157	172	5	9	515	497	8	9	240	254	10	13	167	98	12	2	301	312	8	10	161	92				
1	16	148	153	5	8	154	161	8	8	419	418	10	12	191	232	12	1	143	102	8	6	231	192				
1	15	258	259	5	7	1010	1032	8	6	474	488	10	10	228	229	12	0	333	334	8	2	296	283				
1	14	182	203	5	6	134	107	8	4	350	362	10	8	300	331	11	9	212	223	7	13	224	240				

atoms in the refinement. The final atomic coordinates and vibrational parameters are given in Table 1. Observed and calculated structure factors are tabulated in Table 2.

DESCRIPTION AND DISCUSSION

The coordination around the copper atom is a distorted tetragonal pyramid (Fig. 1) with two nitrogen atoms from imidazole rings and two chlorine atoms lying at the corners of an approximate square as closest ligands to the copper atom. The calculated equation for a least squares plane[11] using these four atomic position is $0.0140x - 0.1849y - 0.9827z - 0.4354 = 0$ and the distances to this plane are for N1 0.085 Å, N3 0.083 Å, Cl1 −0.085 Å, and Cl2 −0.083 Å. The copper atom lies 0.182 Å out of this plane. Through a symmetry operation one of the chlorine atoms (Cl2) is placed at the apex of the pyramidal configuration. In this way infinite chains are formed with this chlorine atom bridging successive copper atoms as is shown in Fig. 1.

In the sixth coordination direction in an imagined octahedral configuration around copper the Cl2 atom is found at a distance of 4.12 Å. Therefore this

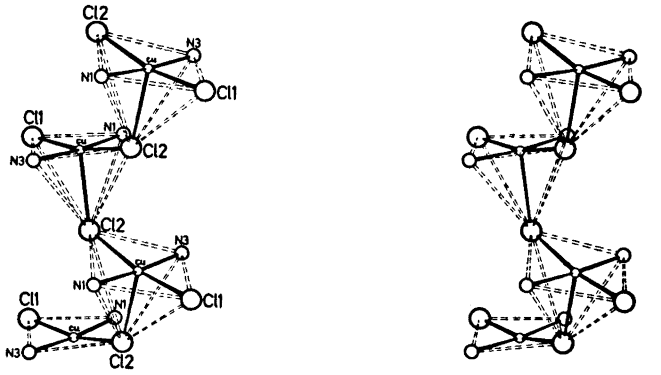

Fig. 1. Stereoscopic illustration of the coordination around copper.

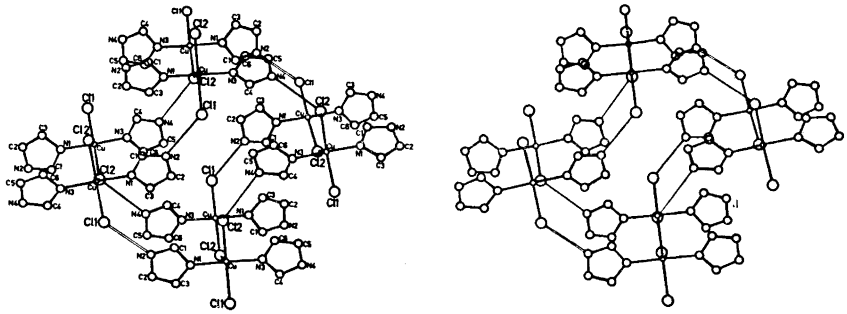

Fig. 2. Stereoscopic illustration of the packing of the polynuclear chains which are held together by means of hydrogen bonds.

structure definitely has a five-coordinated copper atom. The polynuclear chains are held together by hydrogen bonds, N–H···Cl, between symmetry-related chains as shown in Fig. 2. Bond distances and angles are given in Table 3.

Table 3. Bond lengths and bond angles. (Standard deviations for the last significant figure are shown in parentheses.)

(a) Bond lengths (Å)

Cu–Cl1	2.321 (4)	C2–C3	1.339(29)
Cu–Cl2	2.365 (4)	C3–N1	1.376(24)
Cu–Cl2′	2.751 (6)	N3–C4	1.340(31)
Cu–N1	1.973(12)	C4–N4	1.357(27)
Cu–N3	1.992(12)	N4–C5	1.374(28)
N1–C1	1.391(20)	C5–C6	1.321(21)
C1–N2	1.361(20)	C6–N3	1.339(22)
N2–C2	1.381(32)		

(b) Bond angles (°)

Cl1–Cu–Cl2	166.9 (3)	C1–N1–C3	106.9(12)
Cl1–Cu–Cl2′	96.0 (3)	N1–C1–N2	108.0(14)
Cl1–Cu–N1	89.6 (4)	C1–N2–C2	107.5(16)
Cl1–Cu–N3	89.1 (5)	N2–C2–C3	108.8(19)
Cl2–Cu–Cl2′	97.1 (1)	C2–C3–N1	108.7(18)
Cl2–Cu–N1	89.1 (5)	Cu–N3–C4	127.2(15)
Cl2–Cu–N3	90.9 (5)	Cu–N3–C6	126.9(12)
N1–Cu–N3	174.3(10)	C4–N3–C6	104.9(15)
N1–Cu–Cl2′	92.4 (6)	N3–C4–N4	108.9(21)
N3–Cu–Cl2′	93.3 (8)	C4–N4–C5	108.3(17)
Cu–N1–C1	121.2(11)	N4–C5–C6	104.1(15)
Cu–N1–C3	131.9(12)	C5–C6–N3	113.4(16)

Cu–N bond distances. The distances Cu–N1 and Cu–N3 are 1.973(12) Å and 1.992(12) Å, respectively, which are normal bond lengths as can be seen in a paper by Ivarsson, Lundberg and Ingri [2] where Cu–N (imidazole) bond distances which almost all fall in the range 1.95–2.01 Å are tabulated.

Cu–Cl bond distances. The bond lengths to the chlorine atoms lying close to copper in the coordination plane are almost equal (2.321(4) Å and 2.365(4) Å). They are comparable with the Cu–Cl distances found in other complexes in equivalent coordination situations. For example in the triazole complex [12] $C_2N_3H_3 \cdot CuCl_2$ where two nitrogen atoms and two chlorine atoms are lying in the equatorial plane of a distorted octahedron around copper the Cu–Cl distances are 2.337 Å. These distances are close to the sum of the covalent radii for copper and chlorine (2.27 Å) given by Pauling.[13]

The distances from copper to chlorine atoms on one or both sides of the approximately square plane of four ligands vary significantly in different structures. The Cu–Cl bond length to the fifth coordination site is in this determination 2.751(6) Å which is comparable with the distance 2.769 Å in

the above mentioned copper-triazole-chloride complex.[12] It is a little longer than the sum of the ionic radii ($r_{Cu^{2+}} = 0.81$ Å and $r_{Cl^-} = 1.81$ Å) (Pauling 1960, pp. 514, 515[13]) of 2.62 Å. In the structure of catena-μ-imidazolato-chlorido-diimidazolo-copper(II)[1] the chlorine atom lies at the apex of a tetragonal pyramidal configuration just as in this structure but without bridging two copper atoms. In this case the Cu – Cl distance is 2.559 Å.

The imidazole rings. Bond distances and angles which are given in Table 3 are close to the values tabulated by Ivarsson, Lundberg and Ingri,[2] and considering the standard deviations there are no significant differences. The least squares planes of the imidazole rings have the equations:

1st ring (N1, N2, C1, C2, and C3)
$0.0836x + 0.4284y - 0.8997z + 0.6073 = 0$
and 2nd ring (N3, N4, C4, C5, and C6)
$-0.0755x + 0.4537y - 0.8880z + 0.7588 = 0$

The largest deviations from these planes are 0.015 Å (N1) for the first ring and 0.032 Å (C6) for the second ring. The copper atom lies 0.02 Å and 0.14 Å from the planes and is thus characteristically[14] not coplanar with the imidazole rings.

The imidazole rings are not coplanar with a plane through the four closest ligands to copper. In Fig. 2 it can be seen that they are twisted around the Cu – N bonds so as to accommodate space between neighbouring chlorine atoms for the hydrogen atoms of C1, C3, C4, and C6.

Hydrogen bonds. As is also shown in Fig. 2, there are hydrogen bond contacts between symmetry-related polynuclear chains. The hydrogen bond distances N2 – H···Cl1 = 3.158(16) Å and N4 – H···Cl2 = 3.386(17) Å are of the same magnitude as those found in similar structures.[1,15]

Acknowledgements. I express my gratitude to Professor Nils Ingri for his interest and the facilities placed at my disposal. This work forms a part of a programme supported by *Statens Naturvetenskapliga Forskningsråd.*

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Received May 3, 1972.