

Metal Complexes with Mixed Ligands

3. The Crystal Structure of an Imidazolato-bridged Polynuclear Copper(II)-Imidazole Chloride Complex, $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)\text{-}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}$

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The crystal structure of catena- μ -imidazolato-chlorido-diimidazolocopper(II), $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}$, has been determined using three-dimensional X-ray diffraction data. The crystals are orthorhombic, spacegroup $P2_1mn$, with cell dimensions and the corresponding standard deviations: $a = 7.243 \pm 0.001$ Å, $b = 13.726 \pm 0.001$ Å, and $c = 6.096 \pm 0.001$ Å.

There are two formula units per unit cell. The intensities were collected with the Weissenberg equi-inclination technique from two single crystals rotated around the a - and c -axis using a linear diffractometer and $\text{MoK}\alpha$ -radiation. With anisotropic temperature factors for all atoms the refinement converged to a conventional $R = 0.050$. The imidazolato ring is lying in a mirror plane ($y = 0$) with both nitrogens bonded to equivalent copper atoms in the same plane thus forming a bridge between the copper atoms in successive unit cells in the z direction. The two imidazole rings are coordinated to the copper atoms on either side of the mirror plane through one of their nitrogen atoms. The chlorine atom is lying in the mirror plane with the copper-chlorine bond in the x direction. Hence the copper atom is five-coordinated with the bond distances $\text{Cu}-\text{Cl} = 2.559(2)$ Å, $\text{Cu}-\text{N}(\text{C}_3\text{H}_3\text{N}_2^-) = 1.986(5)$ and $1.963(5)$ Å, and $\text{Cu}-\text{N}(\text{C}_3\text{H}_4\text{N}_2) = 2.058(4)$ Å. The polynuclear chains are held together by hydrogen bonds between adjacent chains. The distances $\text{N}-\text{H}\cdots\text{Cl} = 3.223(6)$ Å.

As model compounds for metal-imidazole interactions in biological systems, metal imidazole complexes have been studied both in the solid state and in solution.¹⁻⁷ For $\text{Cu}(\text{II})$ it can be shown that the variation in pH and concentration in preparing copper-imidazole complexes in chloride medium so far has given three different crystalline phases: $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_4\text{Cl}_2$ (under study), $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$ (fully refined), and $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}$, the subject of this communication. This structure was first reported in January 1970 at 7:e Nordiska Strukturkemistmötet in Gothenburg.

EXPERIMENTAL

Crystal preparation and analyses. In a typical preparation 7.5 ml of a 1 M CuCl_2 -solution were added to 92.5 ml of a 1 M $\text{C}_3\text{H}_4\text{N}_2$ -solution and this mixture was divided into ten parts in a set of test-tubes. By adding 0.1 M hydrochloric acid to these tubes the range of pH was adjusted to 7.5–8.0. After a few days at 25°C light blue prismatic crystals of $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}$ were formed. The copper content was determined electrolytically and confirmed using atomic absorption methods. Titration with silver nitrate gave the chloride content and IR-spectra indicated that the crystals contained neither H_2O nor OH^- . (Found: Cu 20.8; N 27.3; C 36.0; H 3.70; Cl 11.5. Calc. for $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}$: Cu 21.0; N 27.8; C 35.8; H 3.67; Cl 11.7.)

The uptake of protons when the crystals were dissolved in an acidic solution of known H^+ -concentration was also measured. This uptake should occur according to the reaction: $\text{Cu}(\text{C}_3\text{H}_3\text{N}_2)(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl} + 4\text{H}^+ = \text{Cu}^{2+} + 3\text{C}_3\text{H}_5\text{N}_2^+ + \text{Cl}^-$. These titrations gave the expected result of four H^+ taken up per copper atom.

Crystal data and space group. From rotation photographs around the *a*- and *c*-axes and the corresponding Weissenberg photographs (*0kl*–*2kl* and *hk0*–*hk2*) taken with $\text{CuK}\alpha$ -radiation it was concluded that the crystals are orthorhombic, that is the Laue group is *mmm*. The only systematic extinctions found were for *hk0*, $h+k=2n+1$ which is characteristic for the space groups *Pmmn* (No. 59) and *P2₁mn* (No. 31).⁸

Precession photographs were taken as a check to confirm the Laue group. The cell dimensions were calculated and refined from a powder photographs giving 75 lines in a focusing camera of Guinier-Hägg type. The following parameters and their corresponding standard deviations were obtained: $a = 7.2427 \pm 0.0008$ Å; $b = 13.7256 \pm 0.0010$ Å; $c = 6.0961 \pm 0.0006$ Å.

The density was determined by the flotation method (using bromoform and acetone) to 1.65 g/cm³. The calculated density with two formula units in the cell is 1.65 g/cm³.

Collection and reduction of intensity data. The intensity data were collected from two different crystals (mounted with the *a*-axis and *c*-axis as rotation axis, respectively) using an automatic linear diffractometer (PAILRED). The radiation used was $\text{MoK}\alpha$ with a LiF-monochromator and pulse height discriminator.

(a) The crystal rotated around the *a*-axis had the dimensions $0.021 \times 0.010 \times 0.013$ cm in the crystallographic *a*, *b*, and *c* directions. The intensities for *0kl*–*6kl* were measured with half scan intervals for *0kl*–*2kl* equal to 0.6° for $\theta > 20^\circ$ and equal to 1.2° for $\theta \leq 20^\circ$. Corresponding values for *3kl*–*6kl* were 0.7° and 1.4°. The scan speed used was 0.5°/min and a weak reflection (counts less than 1000) was measured up to three times. The diffractometer is devised so as to measure a semicircle in reciprocal space which means that equivalent reflections *hkl* and $h\bar{k}\bar{l}$ were both measured. A total of 2700 intensities was obtained in this way. Background radiation was measured during 20 sec on either side of the reflection and the intensity, I_{obs} , for a reflection and the relative counting statistical error of each reflection, $\sigma I/I$, was calculated using the same mathematical expressions as in the paper by Ivarsson, Lundberg and Ingri.⁸

The observed data were reduced so that reflections with negative I_{obs} and/or $\sigma I/I > 0.5$ were omitted. Lp-corrections and absorption corrections were applied and then mean values for identical reflections $F(hkl)$ and $F(h\bar{k}\bar{l})$ were calculated using $\sigma I/I$ as weights.

The intensity data obtained in this way constituted 1101 independent reflections. The linear absorption coefficient is 20.0 cm⁻¹ and the maximum difference in the transmission factor was about 7 %.

(b) The crystal rotated around the *c*-axis had the dimensions $0.022 \times 0.008 \times 0.015$ cm in the crystallographic *a*, *b*, and *c* directions. After reduction of the data as above, 1069 independent reflections were obtained. The maximum difference in the transmission factor was here about 9 %.

(c) A final data set was accomplished after scaling the two sets together, yielding 1385 reflections. (Theoretically about 700 reflections would have been available if $\text{CuK}\alpha$ -radiation had been used.)

Computer programs used. The diffractometer data correction was made by 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 made by a program originally written by P. Coppens, L. Leiserowitz and D. Rabinovich revised by Olle Olofsson and Mats Elfström. The computer program ORTEP⁹ was used to produce the stereoscopic figures. The computers used were CD 3600 and CD 3200.

STRUCTURE DETERMINATION

From experimental data it was concluded that there are two formula units in the unit cell. This means that the copper and chlorine atoms as well as the carbon and nitrogen atoms of the imidazolate ring must be situated in the special twofold positions of the space groups $Pm\bar{m}n$ or $Pm2_1n$ (in the settings $Pm2_1n$ or $P2_1mn$). The twofold positions are

$Pm\bar{m}n$	$Pm2_1n$	$P2_1mn$
(2b) $\frac{1}{4}, \frac{3}{4}, z$ $\frac{3}{4}, \frac{1}{4}, \bar{z}$	(2a) $0, y, z$ $\frac{1}{2}, \frac{1}{2} + y, \bar{z}$	(2a) $x, 0, z$ $\frac{1}{2} + x, \frac{1}{2}, \bar{z}$
(2a) $\frac{1}{4}, \frac{1}{4}, z$ $\frac{3}{4}, \frac{3}{4}, \bar{z}$		

The three-dimensional Patterson synthesis calculated with c -rotation axis data (normalized to $P(0,0,0)=999$) gave a high broad peak at the Harker line $\frac{1}{2}, \frac{1}{2}, \pm 2z$ with $2z \simeq 0.35$ and $P(\frac{1}{2}, \frac{1}{2}, 0.35) = 520$. Such a vector is expected from all the above settings. Two other vectors $P(0.36, 0, 0) = 280$ and $P(0, 0.15, 0) = 126$ with the lengths 2.6 Å and 2.05 Å, respectively, were considered to originate from the vectors between the atoms Cu to Cl and Cu to N(imidazole). The Cu-Cl vector can only be explained if the atoms have positions corresponding to space group $P2_1mn$. Now the copper atom was placed in $x=y=0$ and $z \simeq 0.17$ and the positive x direction chosen so that the coordinates for Cl were $x=0.36, y=0$, and $z=0.17$. Normal Fourier techniques gave the approximate positions of the other atoms although in the early stages there was serious overlapping of the electron density from the atoms of the imidazolate ring.

Structure refinement. Firstly the a - and c -axis data were treated separately, then the data from the two recordings were scaled together to give a total set of data. Every refinement was made with the same full matrix least squares technique. Different schemes of weighting were applied (Hughes and Cruickshank),¹⁰ but in the final refinements all the observed reflections were weighted with $\omega=1$, because the differences in the results were negligible. The atomic scattering factors for carbon, nitrogen, chloride (Cl^-), and copper (Cu^{2+}) were taken from *International Tables*⁸ and account was taken of the real part of the dispersion correction for the copper and chlorine atoms.

The carbon and nitrogen atoms of the imidazole ring which are farthest away from the copper atom could at first not be identified and were both labeled nitrogen. Then the isotropic temperature factor which was higher distinguished the carbon atom. That the right choice was made was checked when looking for a possible hydrogen bond between nitrogen and chlorine.

The isotropic refinements gave the following R -values:

$$(R = \sum ||F_o| - |F_c|| / \sum |F_o|)$$

$R(a\text{-axis})=0.11$ (1101 refl.); $R(c\text{-axis})=0.09$ (1069 refl.); $R(\text{final})=0.11$ (1385 refl.) and after completed anisotropic refinement (H-atoms excluded) the values were $R(a\text{-axis})=0.045$; $R(c\text{-axis})=0.048$; $R(\text{final})=0.050$.

In the last cycle of refinement all parameter shifts were less than 10 % of the corresponding standard deviations. An over-all scale factor was used in all three refinements but individual scale factors were tested in the isotropic refinements of the a -axis and c -axis data. In both these tests the scale factor for the zero layer was lowest with a small increment for successive layers. A reasonable explanation could not be found and any effect on the final observed and calculated structure factors (when over-all scale factor was used) could not be deduced.

In the difference Fourier synthesis the highest peak was about $0.8 \text{ e}^-/\text{\AA}^3$ and some peaks lie where hydrogen atoms are expected to be but there were other peaks equally high in impossible positions, so hydrogen atoms were not included 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

This is one of the few structures,^{6,11} so far determined where both nitrogens of one imidazole ring are coordinated to metal atoms. The imidazolate ring (Im^-) in $\text{Cu}(\text{Im}^-)(\text{ImH})_2\text{Cl}$ acts as a bridge between copper atoms in successive unit cells in the crystallographic z direction. The copper atom and the imidazolate ring as well as the chlorine atom are all lying in the same plane (mirror-plane $y=0$). The Cl atom is lying in the x direction from Cu. Every imidazolate ring has the same orientation so there is no twisting of this group along the chain as there is in copper triazole dichloride.¹² The imidazole groups (ImH) are bonded to the copper atom on either side of the mirror plane through

Table 1. The final atomic positional fractional coordinates and vibrational parameters and their estimated standard deviations (σ in parenthesis). All values multiplied by 10^4 . Anisotropic temperature factors have been calculated according to the formula

$$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	1743 (1)	199 (2)	23(1)	53 (1)	—	28 (5)	—
Cl	3531 (3)	0	1882 (4)	109 (3)	33(1)	196 (6)	—	27 (8)	—
N1	—522 (9)	0	4942 (9)	91(11)	38(3)	84(11)	—	74(17)	—
N2	—510(10)	0	8581 (8)	152(15)	33(3)	54(10)	—	54(17)	—
C1	500(10)	0	6761(10)	123(13)	27(3)	77(10)	—	18(21)	—
C2	—2345(13)	0	7850(13)	127(16)	58(5)	115(16)	—	31(28)	—
C3	—2314(11)	0	5611(12)	89(13)	44(4)	125(15)	—	49(25)	—
N3	—350 (7)	1488(3)	1756 (7)	134(11)	28(2)	143 (8)	15 (6)	23(17)	13 (7)
N4	—1005(10)	3007(4)	860(11)	196(14)	32(3)	313(19)	6(10)	—28(29)	53(12)
C4	—922(11)	2059(5)	139(11)	196(15)	35(3)	205(16)	17(11)	—41(27)	54(12)
C5	—427(12)	3039(5)	2988(13)	240(22)	31(3)	305(21)	—26(12)	0(33)	—4(12)
C6	13(20)	2090(4)	3561 (9)	253(15)	31(2)	207(13)	0(22)	—31(48)	—20 (9)

Table 2. Continued.

K L	K L	K L	K L	K L	K L	K L	K L
H= 5	0 8 69 68	9 7 100 90	1 3 52 49	0 5 84 85	3 2 125 131	3 2 76 82	
	0 7 144 145	9 6 54 47	1 2 221 221	0 4 85 82	3 1 136 136	3 1 62 69	
	0 6 60 65	9 5 92 92	1 1 312 310	0 3 47 39	2 6 54 57	3 0 105 104	
	7 9 56 67	0 5 202 200	0 4 165 167	0 8 95 87	0 2 75 63	2 5 98 101	2 5 73 80
	7 8 85 78	0 4 211 217	9 3 46 33	0 6 139 142	0 1 111 112	2 3 130 130	2 4 87 88
	7 7 54 38	0 3 119 125	9 2 141 142	0 5 128 139		2 2 94 96	2 2 84 90
	7 6 131 138	0 2 159 158	9 1 209 213	0 4 91 98	H= 8	2 1 86 95	2 1 102 111
	7 5 150 150	9 1 328 324	8 8 92 71	0 3 233 230		2 0 129 134	1 6 51 37
	7 3 261 272		8 6 105 102	0 2 223 224		1 5 86 95	1 5 80 87
	7 2 139 142	H= 6	8 5 101 103	0 1 91 95		1 4 113 103	1 3 83 82
	7 1 125 123		8 4 44 42	0 0 205 197		1 3 46 33	1 2 73 74
	7 0 326 333	20 0 54 45	8 3 159 158			1 2 115 116	1 1 47 51
	6 8 68 68	19 4 66 58	8 2 126 133	H= 7		1 1 163 163	1 0 97 96
	6 7 124 126	19 2 65 47	8 1 140 148			0 6 59 64	0 5 74 78
	6 6 52 59	19 1 72 70	8 0 176 196	17 0 43 18		0 5 94 102	0 4 62 58
	6 5 127 134	18 5 63 40	7 8 64 59	16 4 63 36		0 3 146 146	0 2 93 94
	6 4 165 170	18 3 61 59	7 7 117 117	15 4 57 30		0 2 104 114	0 1 107 106
	6 3 79 78	18 2 57 54	7 6 53 50	14 1 49 52			
	6 2 194 194	18 1 51 45	7 5 81 86	13 6 47 41			
	6 1 232 237	18 0 72 76	7 4 191 204	13 1 44 34			
	5 9 68 67	17 5 48 37	7 3 58 60	12 4 51 45			
	5 8 91 85	17 4 80 80	7 2 194 189	12 3 42 16			
	5 6 184 195	17 3 48 21	7 1 214 216	12 2 61 52			
	5 5 125 119	17 2 79 75	6 8 81 77	12 1 47 48			
	5 4 102 114	17 1 74 80	6 6 117 119	11 2 54 41			
	5 3 289 295	16 6 51 51	6 5 118 126	11 0 47 35			
	5 2 159 155	16 5 67 59	6 4 60 56	10 5 54 61			
	5 1 91 97	16 3 76 74	6 3 190 192	10 4 57 54			
	5 0 353 359	16 2 60 57	6 2 151 155	10 2 88 73			
	4 10 69 70	16 1 67 65	6 1 123 124	10 1 54 64			
	4 8 61 59	16 0 67 69	6 0 189 186	9 6 46 41			
	4 7 112 104	15 5 61 53	5 8 55 42	9 4 44 46			
	4 6 55 46	15 4 63 64	5 7 118 111	9 3 43 38			
	4 5 145 144	15 3 44 18	5 6 59 59	8 5 59 51			
	4 4 152 154	15 2 83 82	5 5 111 117	8 4 59 50			
	4 3 163 170	15 1 59 64	5 4 191 199	8 3 77 74			
	4 2 151 150	14 6 66 67	5 3 38 44	8 1 74 73			
	4 1 190 203	14 5 61 60	5 2 193 189	7 6 59 59			
	3 9 62 61	14 4 59 64	5 1 308 309	7 5 75 75			
	3 8 75 77	14 3 97 102	4 8 84 86	7 4 47 21			
	3 7 48 40	14 2 93 94	4 6 120 125	7 3 55 49			
	3 6 125 130	14 1 81 84	4 5 123 126	7 2 71 71			
	3 5 147 146	14 0 93 104	4 4 73 78	6 5 52 61			
	3 4 37 29	13 6 50 32	4 3 193 187	6 4 66 66			
	3 3 238 235	13 5 70 67	4 2 187 194	6 2 79 67			
	3 2 134 124	13 4 124 126	4 1 116 124	6 1 85 84			
	3 1 100 108	13 3 46 38	4 0 199 199	5 5 51 47			
	3 0 302 301	13 2 104 103	3 8 66 61	5 4 52 78			
	2 10 70 71	13 1 130 130	3 7 125 125	5 3 69 57			
	2 9 45 41	12 6 72 77	3 6 64 63	5 2 62 65			
	2 8 78 76	12 5 81 83	3 5 98 99	4 5 75 79			
	2 7 123 122	12 3 117 117	3 4 249 256	4 4 70 71			
	2 6 57 57	12 2 84 87	3 3 66 66	4 2 82 84			
	2 5 102 107	12 1 110 117	3 2 236 237	4 1 92 99			
	2 4 147 151	12 0 138 138	3 1 159 245	3 6 56 55			
	2 3 48 34	11 7 92 83	2 8 98 88	3 5 57 59			
	2 2 292 293	11 5 68 66	2 7 96 30	3 4 59 63			
	2 1 199 210	11 4 141 140	2 6 125 127	3 2 54 54			
	1 9 72 75	11 3 39 29	2 5 130 137	3 1 71 81			
	1 8 139 141	11 1 170 180	2 3 197 197	2 5 62 64			
	1 5 159 156	10 7 50 20	2 2 166 174	2 4 88 72			
	1 4 76 82	10 5 68 66	2 1 202 215	2 2 87 86			
	1 3 340 353	10 4 90 96	2 0 252 246	2 1 93 90			
	1 2 181 177	10 3 64 60	1 8 48 53	1 6 64 55			
	1 1 131 132	10 2 136 135	1 7 131 127	1 4 42 57			
	1 0 448 444	10 1 131 138	1 6 61 64	1 3 69 65			
	0 10 91 86	10 0 77 76	1 5 115 121	1 2 46 52			
	0 9 67 46	10 0 120 123	1 4 230 233	1 1 54 64			

one nitrogen atom completing the tetrahedral pyramidal configuration around copper. In a review of copper complexes by Hatfield and Whyman¹⁸ covering the literature up to 1968, they have listed the approximate coordination to copper for about one hundred crystal structure determinations. Among these 47 are octahedral, 29 are square planar and 21 penta coordinated. The penta-coordination is thus not infrequent. In this structure there is large steric hindrance for another coordinating atom (H₂O could have been expected) to form an octahedral environment around the copper.

In Fig. 3 it can be seen that the polynuclear chains are held together by hydrogen bonds from N4 to chlorine atoms in parallel but symmetry-related chains. The hydrogen bond distances are 3.22 Å. Other interatomic distances between the chains are too long to be van der Waals contacts.

The coordination around Cu. Stereoscopic drawings are given in Fig. 1 and bond lengths and bond angles are given in the schematic drawings of Fig. 2a and b as well as in Table 3. By studying the geometrical features of the surroundings of copper it can be seen that the chlorine atom is placed about 0.09 Å above copper in the z direction. This gives the difference between the angles

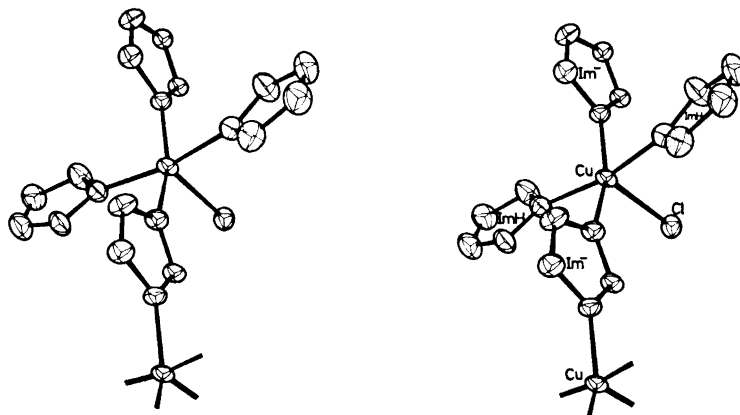


Fig. 1. Stereoscopic diagram of part of the polynuclear chain. Thermal ellipsoids are scaled to enclose 50 % probability.

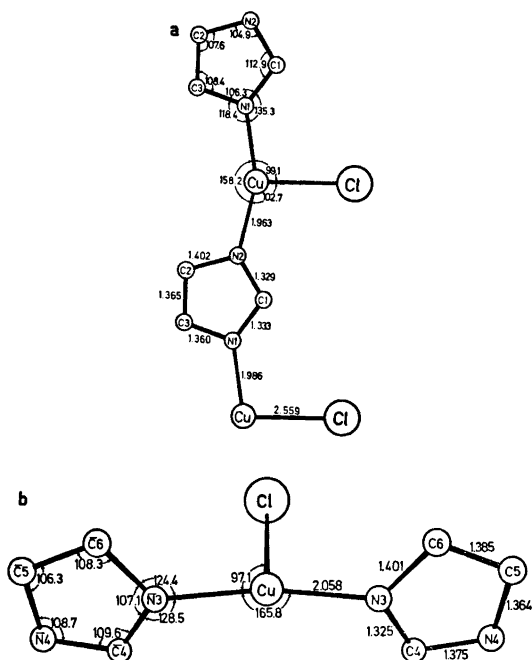


Fig. 2. Schematic drawings showing distances and angles, (a) for the atoms that are lying in the mirror plane (b) for the imidazole rings on either side of the mirror plane.

$\text{Cl}-\text{Cu}-\text{N1} = 99.1^\circ$ and $\text{Cl}-\text{Cu}-\text{N2} = 102.7^\circ$, which together with the angle $\text{N1}-\text{Cu}-\text{N2} = 158.2^\circ$ give a sum of 360.0° . Hence the bonds from copper to the two imidazolite nitrogens are to a considerable degree bent away from

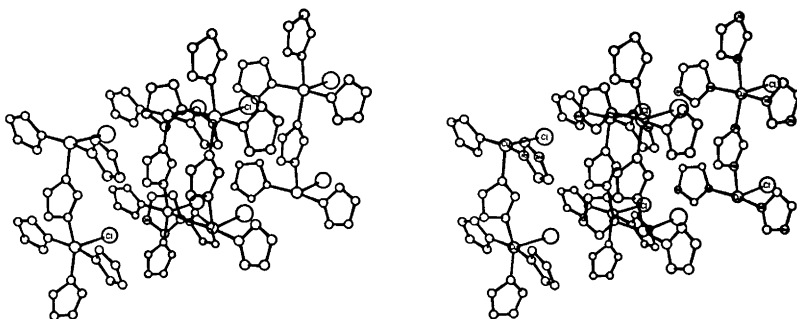


Fig. 3. Stereoscopic diagram of the packing of the polynuclear chains. The atoms labelled N4 are within hydrogen bond contact to chlorine atoms in adjacent chains.

Table 3. Bond lengths and bond angles and their estimated standard deviations. (A = from *a*-axis data; C = from *c*-axis data; Final = from all data.) (a) Bond lengths in Å ($\sigma \times 10^3$ in parentheses).

Bond	A	C	Final
Cu—Cl	2.543 (2)	2.558 (2)	2.559 (2)
Cu—N1	1.989 (4)	1.968 (6)	1.986 (5)
Cu—N2	1.975 (4)	1.963 (6)	1.963 (5)
Cu—N3	2.061 (3)	2.057 (3)	2.058 (4)
N1—C3	1.345(11)	1.378 (9)	1.360(10)
C3—C2	1.373 (7)	1.338(10)	1.365(11)
C2—N2	1.363(11)	1.391 (9)	1.402(12)
N2—C1	1.343 (6)	1.341 (8)	1.329 (9)
C1—N1	1.339 (6)	1.336 (8)	1.333 (9)
N3—C6	1.392 (6)	1.397 (6)	1.401 (7)
C6—C5	1.359 (7)	1.366 (7)	1.385 (9)
C5—N4	1.365 (9)	1.343 (9)	1.364(10)
N4—C4	1.353 (6)	1.356 (7)	1.375 (9)
C4—N3	1.327 (6)	1.327 (7)	1.325 (8)

(b) Bond angles in degrees ($\sigma \times 10$ in parentheses)

Cl—Cu—N1	99.1(2)	C3—C2—N2	107.6(8)
Cl—Cu—N2	102.7(3)	N2—C1—N1	112.9(7)
Cl—Cu—N3	97.1(2)	N1—Cu—N3	88.4(2)
N1—Cu—N2	158.2(3)	N2—Cu—N3	88.9(2)
N3—Cu—N3	165.8(3)	Cu—N3—C4	128.5(4)
Cu—N1—C3	118.4(5)	Cu—N3—C6	124.4(4)
Cu—N1—C1	135.3(5)	C4—N3—C6	107.1(5)
C3—N1—C1	106.3(6)	C4—N4—C5	108.7(6)
Cu—N2—C2	119.4(5)	N3—C4—N4	109.6(6)
Cu—N2—C1	135.8(6)	N3—C6—C5	108.3(6)
C2—N2—C1	104.9(6)	C6—C5—N4	106.3(6)
N1—C3—C2	108.4(8)		

the copper-chlorine bond, the Cu-N1 bond more than the Cu-N2 bond. A least squares plane calculated for Cu, Cl, N3, and $\bar{N}3$ has the equation $0.0287x - 0.9996z - 1.0726 = 0$. The equation shows that this plane is very near parallel to the xy -plane. The largest deviation of the atoms from the calculated plane is for the copper atom which is 0.01 Å above. The bond from copper to the imidazole nitrogens are bent away from the copper-chlorine bond too, the angle Cl-Cu-N3, being 97.1°.

Thus the distorted quadratic arrangement consists of the four nitrogen atoms forming a non-planar square with sides 2.82 Å and the copper atom is 0.25 Å above a line between the two atoms N3. It is 0.38 Å above a line between N1 and N2. The apex of the pyramid is the chlorine atom which is 2.559 Å above the copper atom.

Differences between copper-nitrogen bonds are tabulated and discussed in a paper by Ivarsson, Lundberg and Ingri.⁶ In this structure the difference between a Cu-N(Im⁻) (1.963 and 1.986 Å) bond and a Cu-N(ImH) bond (2.058 Å) is indeed significant and is more pronounced than in other cases showing quite a large flexibility in bond distance between copper and an imidazole nitrogen.

When comparing the bonds from copper to the two nitrogens of the imidazolate ring the bond Cu-N2 is 1.963(5) Å which is more than four standard deviations shorter than the bond Cu-N1 (1.986 Å).

The imidazolate and imidazole rings. Comparisons in Figs. 2a and 2b show that in the imidazolate ring the only significant change from an imidazole ring in bond length, when substituting a hydrogen atom by a copper atom at the nitrogen atom, is the bond between this nitrogen and the carbon atom between the nitrogen atoms (N4 to C4 and N1 to C1) giving equal bond lengths from this carbon atom (C1) to the two nitrogen atoms.

The bond lengths from the metal bonded nitrogens, (N2 and N3), to the other carbon atoms, C2 and C6, are in both cases longer (1.40 Å) than the bond lengths from the "outer" nitrogens, N1 and N4, to corresponding carbon atoms, C3 and C5 (1.36 Å). This seems to be significant when one is trying to show the differences between the nitrogen atoms. The mean values from the determinations in $\text{Cu}_3(\text{Im}^-)_2(\text{ImH})_8(\text{ClO}_4)_4$ ⁶ are for the longer nitrogen-carbon bond 1.39 Å and for the shorter 1.36 Å.

In Table 3 comparisons can be made between the bond distances tabulated after the different refinements. A few significant differences between the determinations *A* and *C* can be seen. Some bond distances for example C2-C3 and N1-C3 show more reasonable values in the calculations based on the final data set compared with other determinations. Bond distances and angles in the imidazolate and imidazole rings are given in Table 3 (see also Fig. 2).

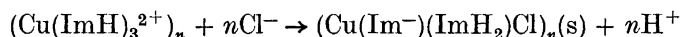
In addition to the specific features already discussed there are no significant deviations from corresponding values tabulated in the paper by Ivarsson Lundberg and Ingri.⁶ The least squares plane calculated for the atoms of the imidazole ring has the equation $0.9413x + 0.1372y - 0.3085z - 0.2770 = 0$ and the largest deviation from this plane is for N3 (0.012 Å).

The copper atom is lying 0.051 Å from the plane and thus characteristically not coplanar with the imidazole ring¹⁹ and the hydrogen bond to a chlorine atom is not in the plane because the Cl atom is lying 1.31 Å from the plane.

Cu-Cl bond length discussion. The distance from copper to chlorine is 2.559(2) Å, which is longer than the sum of the covalent radii (2.27 Å) but close to the sum of the ionic radii ($r_{\text{Cu}^{2+}} = 0.81$ Å and $r_{\text{Cl}^-} = 1.81$ Å) (Pauling 1960, pp. 514, 515)¹⁴ of 2.62 Å. The copper-chlorine bond lengths vary significantly in different structures. If there are two chlorine atoms coordinating to the copper atom on either side of the approximate square plane of four ligands the distances are in bis-biuret-copper(II) dichloride¹⁵ 2.96 Å and in bis-semicarbazide copper(II) chloride¹⁹ 2.85 Å. In the structure of 2-picoline *N*-oxide copper(II) chloride,¹⁷ one copper atom is six-coordinated with the Cu-Cl distance 2.96 Å but the other copper atom is five-coordinated with the relevant Cu-Cl distance equal to 2.65 Å. In this last case the chlorine atom is lying at the apex of a tetrahedral pyramidal configuration around copper just as in this structure determination.

On the formation of imidazolato bridges. Studies in solution by Sjöberg⁷ indicate that at low concentrations and low ratios of imidazole to copper there will be molecular species with hydroxy-bridges at low to medium pH. At higher concentrations these complexes occur at lower pH. When the ratio ImH/Cu is higher (> 4) no such complexes will occur at the pH where the crystals grow. The polynuclear imidazolato-bridged complexes cannot be accounted for in the solution but when crystallization starts during titrations there is an increase in H⁺-concentration. The predominant mononuclear complexes in the solution are at pH 7-8 Cu(ImH)₃²⁺ and Cu(ImH)₄²⁺.

Other mononuclear species that can be accounted for in solution are Cu(ImH)²⁺, Cu(ImH)₂²⁺ and Cu(ImH)₆²⁺. The complex with five ImH ligands to a copper atom is not found. Bridson and Walker¹³ have tried to explain the formation of imidazolato-bridged complexes with a reaction involving hydroxy-bridges. A more reasonable mechanism can be suggested from the results of this structure determination. The formula for the reaction would be



A schematic drawing of this is given in Fig. 4.

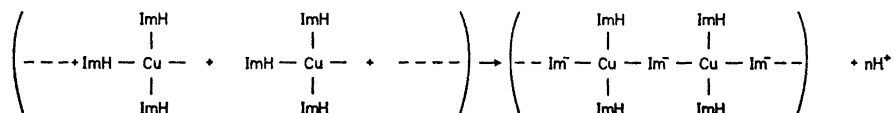


Fig. 4. A schematic drawing of the suggested reaction giving imidazolato bridges.

A possible mechanism for the formation of the trinuclear complex in perchlorate medium determined by Ivarsson, Lundberg and Ingri⁶ could be $2 \text{Cu}(\text{ImH})_3^{2+} + \text{Cu}(\text{ImH})_4^{2+} + 4 \text{ClO}_4^- \rightarrow \text{Cu}_3(\text{Im}^-)_2(\text{ImH})_8(\text{ClO}_4)_4(\text{s}) + 2 \text{H}^+$.

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