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The Crystal Structure of a 1:1 Cupric Nitrate–Pyrazine Complex $Cu(NO_3)_2.(C_4N_2H_4)$

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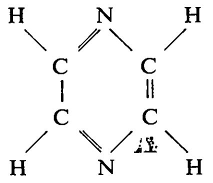
The crystal structure of a 1:1 cupric nitrate–pyrazine complex, $Cu(NO_3)_2.(C_4N_2H_4)$, was determined by single-crystal X-ray diffraction techniques. This compound crystallizes in the orthorhombic system with $a=6{\cdot}712$, $b=5{\cdot}142$, and $c=11{\cdot}732$ Å, space group *Pmna*, $\varrho=2{\cdot}19$ g.cm^{-3} and $Z=2$. The intensities of 642 unique reflections were recorded by the 2θ-scan method and the structure was solved by an analysis of the three-dimensional Patterson map. The structure is a coordination polymer and consists of linear –Cu–pyrazine–Cu–pyrazine– chains. The nitrate groups lie in mirror planes normal to the chain axes and they are coordinated to the Cu^{II} ion unsymmetrically through two oxygen atoms. Refinement by anisotropic least-squares analysis gave an R value of 0·04.

Introduction

Aromatic rings which contain pyridine type nitrogen atoms ($\gt$N) coordinate to transition metal ions. If the coordinating molecule contains more than one pyridine type nitrogen atom, bonding may occur to more than one metal ion to form a polynuclear species. Pyrazine (1,4-diazine)



and $Cu(NO_3)_2$ form an anhydrous crystalline complex with a 1:1 pyrazine to $Cu(NO_3)_2$ ratio. In pyrazine, equivalent nitrogen atoms occupy opposite vertices in the ring and a 1:1 composition suggests chains of the type –pyrazine–Cu–pyrazine–Cu–. As Cu^{II} is generally fourfold or sixfold coordinated, the nitrate groups must be involved in the coordination to the metal ion. The structure analysis of the complex was undertaken to elucidate the features of the copper–ring linkage and to determine the role of the nitrate groups in the coordination about the copper ion.

Experimental

Crystals of $Cu(NO_3)_2.(C_4N_2H_4)$ were grown by evaporation of an aqueous solution of cupric nitrate and pyrazine. Crystal symmetry and approximate cell parameters were determined from zero and upper level precession photographs. Systematic extinctions ($h0l$: $h+l=2n+1$; $hk0$: $h=2n+1$) indicate that the space group is either *Pmna* (No. 53) or *P*2*na* (No. 30). The centric space group was assigned on the basis of the complete structure determination.

To determine precise unit-cell parameters, the 2θ angles of a set of eighteen reflections were measured on a single-crystal diffractometer using molybdenum radiation ($\lambda=0{\cdot}71068$ Å). The cell parameters were then refined by least-squares analysis to obtain the best agreement between the calculated and observed 2θ

angles. Assuming $Z=2$, the X-ray density was found to be 2·19 g.cm^{-3}, in good agreement with the density of 2·15 g.cm^{-3} measured by the flotation method. A summary of the crystal data is given in Table 1.

Table 1. *Crystal data for* $Cu(NO_3)_2.(C_4N_2H_4)$

$a=$ 6·712 (1) Å*	Space group *Pmna*
$b=$ 5·142 (1)	$Z=2$
$c=$11·732 (2)	$\varrho_o=$2·15 g.cm^{-3}
$\mu=$27·3 cm^{-1}	$\varrho_c=$2·19

Systematic extinctions

$h0l$: $h+l=2n+1$

$hk0$: $h=2n+1$

* The numbers in parentheses are standard deviations obtained from a least-squares refinement using 18 experimental 2θ values.

Intensities were measured by the 2θ scan method with Mo $K\alpha$ radiation. The rate of scanning was 2° min^{-1}, and the scan range (SR) was calculated using the equation SR$=2·1+1·0\tan\theta$. The backgrounds were measured for 30 seconds at $2\theta\pm\frac{1}{2}$SR. The crystal used for intensity measurements was approximately a parallelepiped of length 0·25 mm and cross-section 0·046 × 0·023 mm. The intensities of six standard reflections, measured periodically along with the data, held constant to within 1%. A standard deviation (σ) was calculated for each intensity and if the net number of counts did not exceed 2σ the reflection was considered unobserved and its intensity was set equal to σ. In the 2θ range 0–60°, 1089 reflections were recorded. These reflections were averaged to obtain a unique set of 642 reflections of which 217 were labelled unobserved. The intensity data were corrected for Lorentz and polarization factors but in view of the small size of the crystal no absorption correction was applied.

Determination

As indicated above, there are two molecules of $Cu(NO_3)_2.(C_4N_2H_4)$ per unit cell. If the centrosymmetric space group is assumed, the nitrogen atoms and all or some of the oxygen atoms must lie on special position m or 2 and the positions of the copper atoms must have symmetry $2/m$. These positions account for the observation that the hkl reflections with $h+l$ even are significantly stronger than those with $h+l$ odd.

A three-dimensional Patterson map was calculated using the complete set of data. The analysis of this map showed that all the principal vectors could be accounted for by placing the copper atom at the origin, the oxygen and nitrogen atoms of the nitrate groups on special positions m, the nitrogen atoms of the pyrazine ring on special positions 2(e), and the carbon atoms on general positions. Thus the complete structure is specified by one copper atom, one nitrate group, and by one carbon atom and one nitrogen atom in the pyrazine ring.

Refinement

The model derived from the Patterson map was refined by full-matrix least-squares analysis. The quantity minimized was $\sum w(F_o-F_c)^2$ with the weighting scheme $w=1$ for $F_o\le 30$ and $w=30/F_o$ for $F_o>30$. The F_o of an unobserved reflection was weighted zero or one depending on whether F_c was less or greater than the assigned value of F_o. The scattering factors used in the structure factor calculations are those given in *International Tables for X-ray Crystallography* (1962) for neutral nickel, nitrogen, carbon and hydrogen atoms and for the (O$^-$) oxygen atom. After 3 cycles of isotropic refinement, the R index

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

based on 425 observed reflections was 0·092.

A difference Fourier synthesis calculated at this point showed that the largest peaks corresponded to the hydrogen atoms in the pyrazine molecule. The model including hydrogen atoms was then refined and after 3 cycles of full-matrix anisotropic least-squares analysis the R index was 0·040. In this refinement, the positional parameters of the hydrogen atom were treated as variables but a fixed isotropic temperature factor of 3·5 was assigned. The average shift/error for the 46 refined parameters was 0·09. As the refinement of the trial model was satisfactory in the space group *Pmna*, no further consideration was given to the acentric space group. The final positional and thermal parameters are presented in Tables 2 and 3, and the structure factors are given in Table 4.

Table 2. *Atomic coordinates*

	x	y	z
Cu	0	0	0
C	0·39666 (56)*	0·16649 (83)	−0·06476 (35)
H	0·324 (12)	0·288 (14)	−0·1064 (57)
N(1)	0·29566 (55)	0	0
N(2)	0	0·26258 (102)	0·19356 (42)
O(1)	0	0·01767 (87)	0·17111 (31)
O(2)	0	0·41383 (100)	0·11029 (42)
O(3)	0	0·33353 (106)	0·29226 (40)

* The numbers in parentheses are standard deviations in the last significant figures.

Description and discussion

The structure of $Cu(NO_3)_2.(C_4N_2H_4)$ consists of linear –Cu–pyrazine–Cu–pyrazine– chains with nitrate anions bonded to the copper atoms unsymmetrically through two oxygen atoms. One such chain is shown schematically in Fig. 1. The detailed structure viewed along the c axis is shown in Fig. 2. The projection of the structure along the polymer axis is given in Fig. 3. These Figures show that the pyrazine–copper chains lie on twofold axes parallel to the crystallographic a

axis, that the nitrate groups lie in mirror planes normal to the axis of the chains, and that the copper atoms occupy $2/m$ sites. Consequently the four carbon atoms and two nitrogen atoms in the pyrazine rings are coplanar. The details of the copper coordination polyhedron are shown in Fig. 4. Fig. 5 shows the pyrazine molecule and nitrate group. All unique bond distances and angles are included in the Figures, and these values, with e.s.d.'s, are given in Table 5.

The coordination polyhedron about the cupric ion is a distorted octahedron which consists of two nitrogen atoms and four oxygen atoms (Fig. 4). Two of the oxygen atoms and the two nitrogen atoms describe a nearly square parallelogram with the cupric ion at its center approximately 2 Å from the four ligands. The two remaining oxygen atoms are considerably further from the metal ion (~2·5 Å). Copper(II) forms a wide variety of sixfold coordinated complexes with approximately tetragonal coordination symmetry. The combination of four short and two long bonds is most commonly observed. The stereochemistry of octahedrally coordinated cupric ion complexes has been

Table 3. *Anisotropic thermal parameters* (× 10^5)

The general anisotropic temperature factor has the form $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	365 (15)*	1955 (34)	222 (6)	0	0	−172 (16)
C	588 (71)	2204 (139)	418 (25)	4 (88)	−68 (35)	132 (54)
N(1)	506 (67)	2086 (140)	251 (22)	0	0	−150 (73)
N(2)	1228 (106)	2129 (180)	233 (30)	0	0	−68 (63)
O(1)	1134 (74)	1624 (135)	292 (23)	0	0	−71 (59)
O(2)	2066 (127)	2249 (158)	473 (34)	0	0	141 (64)
O(3)	3353 (173)	3061 (204)	317 (31)	0	0	−390 (73)

* The numbers in parentheses are standard deviations in the last significant figures. An isotropic B (3·5) was assumed for the hydrogen atom.

Table 4. *Observed and calculated structure factors* (× 10)

The columns are h, k, F_o, F_c respectively.

Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation are marked by an L. The value assigned to the observed intensity for these reflections is equal to one standard deviation.

L = 0			
2	0	1247	1340
4	0	718	699
6	0	419	399
8	0	284	286
0	1	848	838
2	1	283	280
4	1	312	308
6	1	230	229
8	1	177	176
0	2	478	490
2	2	293	299
4	2	433	448
6	2	279	288
8	2	105	124
0	3	574	569
2	3	414	439
4	3	515	522
6	3	327	338
8	3	115	122
0	4	326	327
2	4	218	223
4	4	311	305
6	4	215	225
0	5	320	319
2	5	186	193
4	5	169	171
6	5	124	126
0	6	212	202
2	6	115	96
4	6	49L	63
0	7	176	165
2	7	106	102
L = 1			
1	0	572	545
3	0	889	899
5	0	461	469
7	0	340	344
9	0	86	99
0	1	400	-425
1	1	302	298
2	1	410	-419
3	1	535	549
4	1	260	-247
5	1	280	281
6	1	105	-120
7	1	266	272
8	1	45L	-33
9	1	90	100
0	2	351	357
1	2	607	614
2	2	233	229
3	2	469	481
4	2	59	59
5	2	180	184
6	2	42L	14
7	2	244	249
8	2	47L	26
9	2	149	150
0	3	34L	-44
1	3	457	462
2	3	37L	-28
3	3	337	338
4	3	54	-6
5	3	89	95
6	3	44L	0
7	3	194	206
8	3	50L	5
0	4	108	-101
1	4	285	292
2	4	70	-69
3	4	262	268
4	4	43L	-11
5	4	119	107
6	4	46L	-2
7	4	172	171
0	5	56	-70
1	5	188	189
2	5	43L	-50
3	5	237	242
4	5	45L	-18
5	5	149	149
6	5	50L	-16
0	6	45L	-11
1	6	45L	38
2	6	46L	-9
3	6	130	124
4	6	49L	-6
5	6	98	91
0	7	49L	9
1	7	99	85
2	7	50L	0
L = 2			
0	0	593	519
2	0	74	-52
4	0	110	107
6	0	136	118
8	0	129	126
0	1	801	791
1	1	367	-361
2	1	282	278
3	1	40	-42
4	1	305	298
5	1	40L	13
6	1	211	204
7	1	43L	-25
8	1	133	138
9	1	50L	-59
0	2	573	605
1	2	40L	-42
2	2	317	338
3	2	72	80
4	2	415	414
5	2	96	102
6	2	266	271
7	2	44L	26
8	2	122	123
9	2	57	-28
0	3	121	123
1	3	86	-98
2	3	52	59
3	3	74	-65
4	3	243	247
5	3	42L	-27
6	3	184	186
7	3	47L	-9
8	3	69	64
0	4	192	201
1	4	115	106
2	4	100	97
3	4	42L	20
4	4	177	180
5	4	45L	-32
6	4	111	129
7	4	50L	-1
0	5	259	251
1	5	42L	-47
2	5	139	137
3	5	76	-83
4	5	134	135
5	5	80L	-85
6	5	98	100
0	6	160	158
1	6	45L	-12
2	6	68	70
3	6	47L	-11
4	6	74L	65
5	6	51L	-9
0	7	97	100
1	7	49L	-1
2	7	50L	47
L = 3			
1	0	29L	-29
3	0	270	277
5	0	124	116
7	0	188	177
9	0	50L	52
0	1	442	435
1	1	174	174
2	1	143	143
3	1	367	361
4	1	64	-63
5	1	160	159
6	1	41L	-36
7	1	213	215
8	1	46L	40
9	1	87	89
0	2	204	203
1	2	213	228
2	2	82	73
3	2	305	281
4	2	65	-65
5	2	99	112
6	2	42L	-41
7	2	207	202
8	2	48L	36
0	3	136	-130
1	3	259	271
2	3	120	-103
3	3	249	251
4	3	70	-69
5	3	100	76
6	3	45L	-39
7	3	153	157
8	3	51L	-18
0	4	41L	37
1	4	102	92
2	4	62	73
3	4	135	134
4	4	107	121
5	4	45L	36
6	4	83	76
7	4	105	109
0	5	74	-73
1	5	85	64
2	5	44L	-28
3	5	122	124
4	5	46L	43
5	5	48L	60
6	5	50L	36
0	6	45L	0
1	6	102	111
2	6	46L	0
3	6	158	147
4	6	50L	2
0	7	49L	49
1	7	49L	20
L = 4			
0	0	449	448
2	0	169	167
4	0	307	296
6	0	214	210
8	0	118	117
0	1	654	645
1	1	197	-176
2	1	297	297
3	1	74	65
4	1	366	366
5	1	132	127
6	1	248	247
7	1	66L	39
8	1	138	132
9	1	51L	-30
0	2	351	342
1	2	46	52
2	2	91	115
3	2	159	162
4	2	217	221
5	2	145	146
6	2	179	167
7	2	45L	37
8	2	88	95
0	3	390	385
1	3	87	-60
2	3	205	221
3	3	42L	-52
4	3	242	245
5	3	43L	-33
6	3	157	166
7	3	48L	-17
8	3	95	96
0	4	276	283
1	4	105	96
2	4	151	159
3	4	42L	7
4	4	181	189
5	4	45L	-34
6	4	136	138
7	4	51L	16
0	5	146	139
1	5	145	146
2	5	44L	56
3	5	83	61
4	5	101	100
5	5	49L	7
6	5	85	83
0	6	155	160
1	6	46L	16
2	6	97	98
3	6	70	15
4	6	127	117
0	7	50L	61
L = 5			
1	0	389	398
3	0	372	347
5	0	167	157
7	0	268	253
9	0	163	162
0	1	218	217
1	1	723	715
2	1	89	76
3	1	616	605
4	1	58L	-58
5	1	268	266
6	1	43L	-34
7	1	275	277
8	1	48L	39
0	2	173	168
1	2	261	269
2	2	75	54
3	2	367	366
4	2	60L	-58
5	2	172	171
6	2	44L	-37
7	2	205	202
8	2	49L	31
0	3	65	52
1	3	188	199
2	3	65	38
3	3	301	306
4	3	42L	33
5	3	198	191
6	3	46L	21
7	3	201	202
8	3	51L	11
0	4	42L	-50
1	4	318	327
2	4	42L	-1
3	4	345	350
4	4	68	70
5	4	215	209
6	4	49L	50
7	4	200	199
0	5	44L	14
1	5	139	140
2	5	44L	42
3	5	145	155
4	5	82	83
5	5	83	67
6	5	51L	57
0	6	47L	24
1	6	119	111
2	6	48L	17
3	6	120	109
4	6	51L	17
L = 6			
0	0	527	523
2	0	375	376
4	0	508	496
6	0	336	334
8	0	143	141
0	1	658	641
1	1	42	25
2	1	415	433
3	1	72	80
4	1	466	463
5	1	77	69
6	1	310	307
7	1	45L	1
8	1	146	147
0	2	528	515
1	2	234	-224
2	2	267	282
3	2	68	-71
4	2	267	265
5	2	42L	0
6	2	193	188
7	2	65	-10
8	2	138	131
0	3	520	513
1	3	140	142
2	3	301	295
3	3	106	114
4	3	237	232
5	3	89	67
6	3	174	163
7	3	50L	46
0	4	402	403
1	4	42L	42
2	4	269	257
3	4	43L	-15
4	4	226	229
5	4	47L	-41
6	4	176	165
7	4	52L	-2
0	5	157	165
1	5	44L	-7
2	5	96	102
3	5	46L	-34
4	5	148	153
5	5	50L	-43
0	6	129	122
1	6	48L	17
2	6	73	90
3	6	50L	22
4	6	141	142
L = 7			
1	0	581	574
3	0	395	394
5	0	124	106
7	0	197	207
0	1	36L	-21
1	1	333	337
2	1	50L	-32
3	1	320	313
4	1	42L	-58
5	1	123	117
6	1	44L	-36
7	1	207	204
8	1	50L	-2
0	2	39L	-26
1	2	279	269
2	2	41L	-51
3	2	373	370
4	2	56L	-52
5	2	226	222
6	2	56	-25
7	2	219	220
8	2	50L	1
0	3	131	130
1	3	221	222
2	3	106	105
3	3	335	339
4	3	75	83
5	3	231	223
6	3	76	52
7	3	179	186
0	4	97	-101
1	4	97	96
2	4	81	-77
3	4	188	179
4	4	45L	-29
5	4	126	109
6	4	50L	-17
0	5	44L	-23
1	5	155	151
2	5	45L	-18
3	5	140	146
4	5	49L	0
5	5	94	60
0	6	48L	22
1	6	161	156
2	6	49L	10
3	6	136	122
L = 8			
0	0	127	131
2	0	40L	64
4	0	273	264
6	0	182	192
8	0	51L	46
0	1	216	214
1	1	39L	-4
2	1	92	109
3	1	42L	-5
4	1	237	236
5	1	43L	-1
6	1	179	173
7	1	46L	4
8	1	67L	70
0	2	473	466
1	2	52L	21
2	2	281	267
3	2	42L	7
4	2	243	234
5	2	44L	-12
6	2	164	164
7	2	49L	-5
0	3	274	273
1	3	42L	17
2	3	106	95
3	3	43L	14
4	3	45L	70
5	3	46L	0
6	3	73	63
7	3	51L	6
0	4	162	160
1	4	44L	-55
2	4	44L	48
3	4	45L	-35
4	4	47L	62
5	4	49L	-19
6	4	51L	53
0	5	154	154
1	5	46L	32
2	5	108	103
3	5	48L	36
4	5	145	149
5	5	51L	24
0	6	75	48
1	6	49L	-8
2	6	50L	31
L = 9			
1	0	258	254
3	0	206	209
5	0	44L	35
7	0	150	155
0	1	101	104
1	1	171	164
2	1	112	115
3	1	174	172
4	1	118	118
5	1	44L	39
6	1	94	77
7	1	140	135
0	2	88	-81
1	2	163	163
2	2	55	-49
3	2	244	243
4	2	43L	12
5	2	145	136
6	2	48L	18
7	2	146	151
0	3	43L	-37
1	3	43L	28
2	3	43L	-38
3	3	161	161
4	3	45L	-19
5	3	119	107
6	3	50L	-11
0	4	83	95
1	4	102	73
2	4	45L	63
3	4	124	136
4	4	48L	28
5	4	50L	70
0	5	67	61
1	5	131	123
2	5	48L	36
3	5	114	116
4	5	50L	15
0	6	50L	14
1	6	50L	45
L = 10			
0	0	429	437
2	0	304	312
4	0	359	359
6	0	244	242
0	1	182	181
1	1	94	100
2	1	90	83
3	1	43L	22
4	1	172	175
5	1	60	-22
6	1	140	136
7	1	50L	8
0	2	220	215
1	2	56L	68
2	2	88	89
3	2	43L	5
4	2	131	117
5	2	46L	-28
6	2	103	94
7	2	51L	8
0	3	328	318
1	3	43L	2
2	3	188	178
3	3	45L	2
4	3	159	154
5	3	49L	-2
6	3	117	114
0	4	171	189
1	4	46L	40
2	4	111	102
3	4	74	76
4	4	111	122
5	4	77	71
0	5	110	105
1	5	48L	-5
2	5	49L	62
3	5	50L	36
L = 11			
1	0	341	333
3	0	317	322
5	0	154	168
7	0	204	203
0	1	177	-174
1	1	227	222
2	1	110	-116
3	1	245	244
4	1	45L	-15
5	1	130	124
6	1	66L	0
0	2	57	55
1	2	168	175
2	2	68	82
3	2	222	218
4	2	108	117
5	2	126	116
6	2	79	75
0	3	44L	29
1	3	200	191
2	3	45L	23
3	3	223	229
4	3	48L	28
5	3	110	132
0	4	47L	69
1	4	149	146
2	4	47L	29
3	4	178	171
4	4	50L	-7
0	5	49L	61
1	5	111	119
2	5	50L	24
L = 12			
0	0	220	213
2	0	116	109
4	0	155	150
6	0	133	119
0	1	347	346
1	1	44L	-9
2	1	231	228
3	1	45L	-64
4	1	233	231
5	1	76L	-82
6	1	172	165
0	2	293	295
1	2	95	94
2	2	192	195
3	2	46L	25
4	2	210	213
5	2	49L	-14
0	3	177	173
1	3	46L	9
2	3	99	103
3	3	48L	15
4	3	150	148
5	3	51L	13
0	4	170	174
1	4	48L	-3
2	4	108	113
3	4	50L	42
L = 13			
1	0	45L	68
3	0	142	142
5	0	51L	81
0	1	45L	-6
1	1	170	170
2	1	45L	18
3	1	210	213
4	1	65	54
5	1	123	124
0	2	45L	-55
1	2	167	165
2	2	46L	-26
3	2	182	181
4	2	49L	25
5	2	94	91
0	3	47L	0
1	3	130	143
2	3	48L	-8
3	3	136	137
4	3	51L	-4
0	4	80	65
1	4	91	95
2	4	50L	30
L = 14			
0	0	195	194
2	0	93	82
4	0	77	72
0	1	177	180
1	1	47L	45
2	1	91	86
3	1	49L	16
4	1	89	100
0	2	93	105
1	2	48L	24
2	2	48L	49
3	2	49L	0
4	2	103	107
0	3	117	103
1	3	49L	-13
2	3	49L	64
3	3	51L	-5
L = 15			
1	0	48L	39
3	0	108	126
0	1	48L	13
1	1	94	82
2	1	49L	18
3	1	120	133
0	2	49L	12
1	2	91	73
2	2	50L	10
0	3	50L	18

Table 5. *Bond distances and angles*

	Distance		Angle
Coordination sphere			
Cu–N(1)	1·984 (4) Å*	N(1) Cu O(1) or O(2)	90°
Cu–O(1)	2·010 (4)		
Cu–O(2)	2·490 (5)	O(1) Cu O(2)	56·11 (17)
Nitrate group			
N(2)–O(1)	1·287 (7)	O(1) N(2) O(2)	116·71 (48)
N(2)–O(2)	1·249 (7)	O(1) N(2) O(3)	119·30 (50)
N(2)–O(3)	1·214 (7)	O(2) N(2) O(3)	123·99 (55)
Pyrazine molecule			
N(1)–C(1)	1·330 (5)	C(1) N(1) C(1′)	118·73 (36)
C(1)–C(1′)	1·387 (5)	N(1) C(1) C(1′)	120·64 (37)
C(1)–H(1)	0·93 (7)		

* The numbers in parentheses are the standard deviations in the last significant figure.

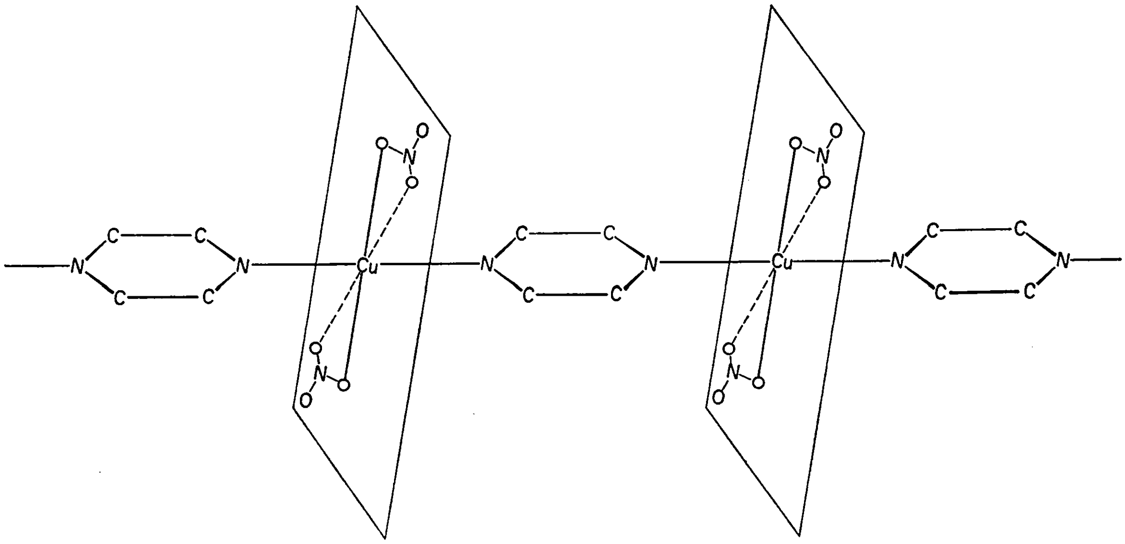


Fig. 1. Schematic diagram of the linear-coordination polymer, $Cu(NO_3)_2.(C_4N_2H_4)$. The chain axis is perpendicular to the planes which contain the copper atoms and nitrate groups.

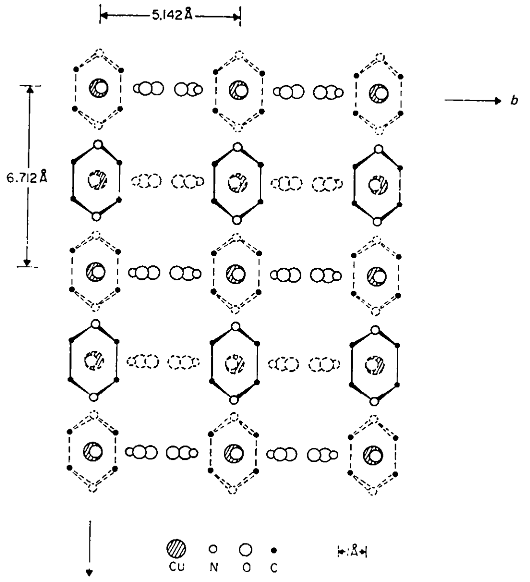


Fig. 2. Projection of the structure along the *c* axis.

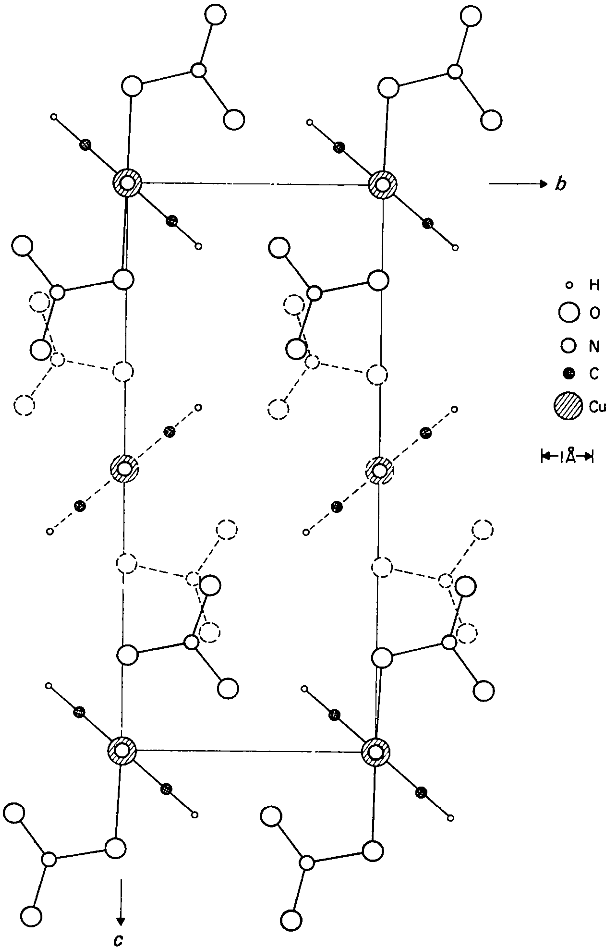


Fig. 3. Projection of the structure along the polymer axis (*a* axis).

discussed by Orgel & Dunitz (1957). Also a number of complexes of copper(II) exist in which the bonding in the *xy* plane is very strong and the electron density in the d_{z^2} orbital is raised sufficiently so that no bonding occurs along the *z* axis. The result is a square-planar complex. For example, in the complex copper bis-(dimethylglyoxime) (Bezzi, Bua & Schiavinato, 1951) the Cu–N distance is 1·92 Å and in bis(salicylaldiminato)copper(II) (Stewart & Lingafelter, 1959) the Cu–O and Cu–N distances are ~1·84 Å.

In the present case, the bonding in the *xy* plane is not very strong as evidenced by the Cu–N (1·984 Å) and Cu–O (2·010 Å) distances. Thus a complex with four short and two long bonds rather than a square-planar complex is most consistent with the *xy* bond distances. A simple elongation of the type described by Orgel & Dunitz (1957), however, cannot occur when the nitrate group acts as a bidentate ligand because of the constraint imposed by the geometry of the nitrate group. As a result of this constraint, the elongation must be accompanied by a large angular deviation (~34°) from perpendicularity with the plane of the other four atoms. This unsymmetrical bidentate coordination of the nitrate group is clearly reflected in the N–O bond distances. The strongly bound O(1) atom has an N(2)–O(1) distance of 1·287 Å, while weakly bound O(2) has an N(2)–O(2) distance of 1·249 Å. This difference, coupled with the fact that the N(2)–O(2) distance is significantly longer than the distance between N(2) and the unbound oxygen atom O(3) indicates that O(2) is actually coordinated to the copper(II) ion. The latter conclusion is also supported by the fact that there is no prohibition on the position of the nitrate group which would preclude sufficient rotation to allow only O(1) to bond in a square-planar complex. It should also be noted that a symmetrical bidentate coordination of the nitrate group could have been achieved with reasonable Cu–O distances (1·95–2·00 Å) and with $\mathrm{Cu}\overset{\mathrm{O}}{\underset{\mathrm{O}}{<}}$ angle of 60–70°. The angular distortion in that case would have been no larger than the distortion actually observed (~34°). Thus it appears that the d_{z^2} orbital destabilization provides the most consistent account for the markedly unsymmetrical coordination of the nitrate groups.

The bond distances and angles observed in coordinated pyrazine can be compared with those observed in molecular pyrazine (Wheatley, 1957). This comparison is especially appropriate because, in both structures, the pyrazine rings have $2/m$ symmetry with the twofold axis passing through the two nitrogen atoms. The bond distances observed in coordinated pyrazine (C–C, 1·387; C–N, 1·330 Å) are in substantial agreement with those (C–C, 1·378; C–N, 1·334 Å) reported by Wheatley. However, the $\mathrm{N}\overset{\mathrm{C}}{\underset{\mathrm{C}}{<}}$ angle of 118·7° in the coordinated ring is significantly greater

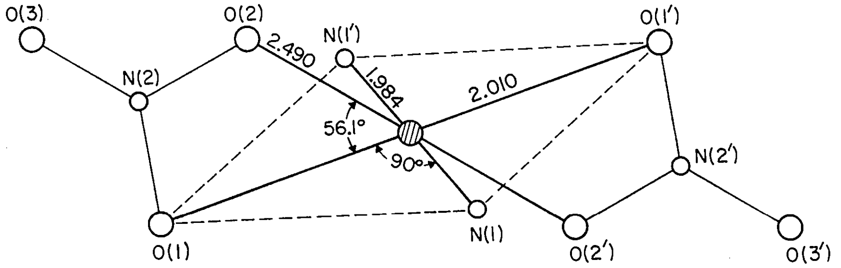


Fig. 4. Details of the Cu^{II} coordination. Unique bond distances and angles are indicated.

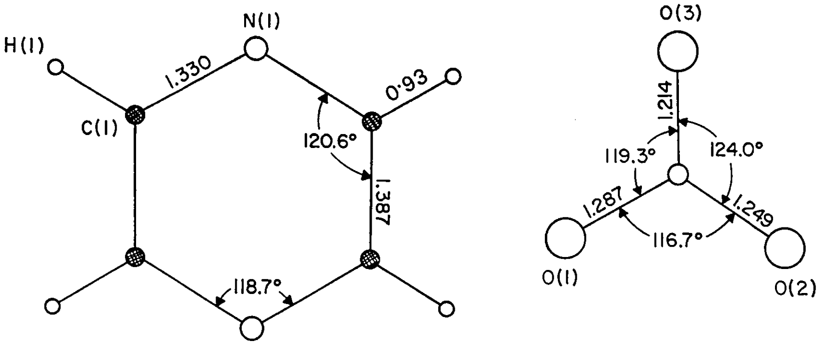


Fig. 5. The coordinated pyrazine molecule and the nitrate group. Unique bond distances and angles are indicated.

than the corresponding $\mathrm{N}{<}^{\mathrm{C}}_{\mathrm{C}}$ angle (~115°) found in both molecular pyrazine and in molecular 1,3-diazine (Wheatley, 1960). This increase in the $\mathrm{N}{<}^{\mathrm{C}}_{\mathrm{C}}$ angle when pyrazine is coordinated is probably due to the involvement of the lone-pair electrons on the nitrogen atom in bonding to the copper atom which reduces the repulsion between lone-pair and ring electrons.

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