899. *Molecular Complexes. Part III.* The Crystal and Molecular Structure of the* 1 : 2 *Molecular Compound of Bis-*8*-hydroxyquinolinatocopper*(II) *and Picryl Azide*

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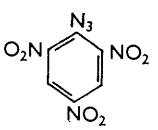
The crystal structure of the molecular complex of bis-8-hydroxyquinolinatocopper(II) and picryl azide has been determined by three-dimensional *X*-ray methods. In the crystal, the picryl azide molecules occupy the positions predicted by the overlap and orientation principle. The copper atom is truly four-co-ordinate, the next nearest neighbours being four nitro-group oxygen atoms at 3·78 Å; the azide group is non-linear.

Bis-8-hydroxyquinolinatocopper(II) and the palladium analogue form a number of highly coloured compounds with various aromatic " electron-acceptor " molecules, such as 1,3,5-trinitrobenzene, picryl azide (I), and benzotrifurazan, in which there are two " acceptor " molecules to one molecule of the metal derivative. Whilst it is not impossible that these are six-co-ordinate copper co-ordination complexes, there is strong spectroscopic evidence that they are of the " polarisation bonded " or " charge-transfer " type. The compound chosen for *X*-ray investigation was the picryl azide adduct of bis-8-hydroxyquinolinatocopper(II) because of the excellent quality of the crystals, and because of some intrinsic interest in the picryl azide molecule. The crystals are intensely coloured magenta-red pleochroic needles, stable in air, but decomposed after prolonged exposure to *X*-rays.



(I)

Crystal Data.—$H_{16}C_{40}CuN_{14}O_{14}$, $M = 860{\cdot}1$. Monoclinic prismatic $a = 16{\cdot}14 \pm 0{\cdot}04$, $b = 30{\cdot}93 \pm 0{\cdot}08$, $c = 6{\cdot}90 \pm 0{\cdot}02$ Å, $\gamma = 105{\cdot}6° \pm 0{\cdot}2°$; $U = 3320{\cdot}8$ Å^3. $D_m = 1{\cdot}709$,

* Part II, B. Kamenar, C. K. Prout, and J. D. Wright, preceding Paper.

$Z = 4, D_c = 1{\cdot}718$. $F(000) = 1980$. Space group $A2/a$ (C^6_{2h}, No. 15, equivalent positions x,y,z; $\frac{1}{2}+x,y,-z$; $x,\frac{1}{2}+y,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}+y\,\frac{1}{2}-z$; plus centre). Cu-$K_\alpha$ radiation, $\mu = 20{\cdot}96$ cm.$^{-1}$, single-crystal oscillation and Weissenberg photographs. Optically biaxial.

The non-standard space-group setting was used for computational convenience. The space group requires that the copper atom should be at a special four-fold position, either at a centre of symmetry or on a two-fold axis. The bis-8-hydroxyquinolinatocopper(II) molecule must therefore have a centre of symmetry or a two-fold axis; either is consistent with a planar molecule.

A three-dimensional Patterson function " sharpened to point atoms at rest " was computed from 1149 independent reflections. The distribution could only be interpreted on the assumption that the copper atom was on the two-fold axis at 1/4, 0,z, with z approximately 1/12, Minor peaks indicated positions for all light atoms except hydrogen.

The structure was refined by the method of least-squares by using a block-diagonal approximation to the normal matrix. Seven cycles were calculated. For the first three cycles, unit weights and isotropic temperature factors were assumed. After the third cycle, hydrogen-atom positions were estimated and included in the calculation, the weighting function

$$\sqrt{\omega} = \sqrt{\frac{1}{1+\left(\frac{|F_o|-b}{a}\right)^2}}$$

with $a = 30$ and $b = 107$ on same scale as Table 1 was used, and anisotropic thermal motion was taken into account. The final reliability factor was 0·134 for observed terms.

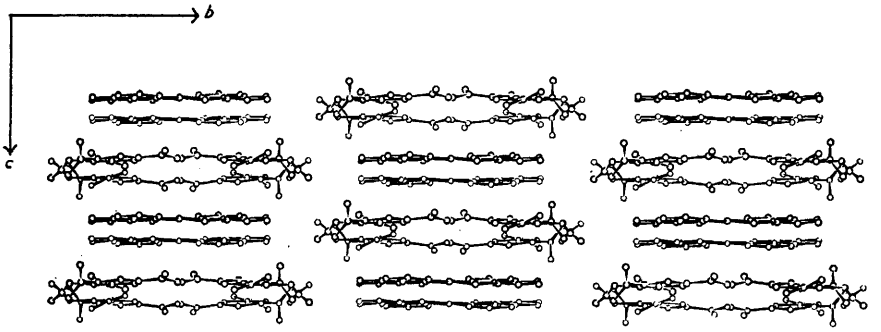


FIGURE 1. The crystal structure projected down the a axis. The atoms outlined by the thicker circles are those of molecules nearer the viewer

Table 1 lists the observed and calculated structure factors based on the final atomic co-ordinates given in Table 2. The standard deviations are minimum values deduced from the block-diagonal approximation to the normal matrix. The thermal parameters are given in Table 3 and the atomic co-ordinates (in Å) referred to the orthogonal axes a, b^*, c, in Table 4. Interatomic distances with standard deviations derived from the formula of Cruickshank and Ahmed[1] are listed in Table 5. Inter-bond angles are shown in Figure 3. Their standard deviations according to the formula of Darlow[2] are about 1—2°.

The crystals contain isolated bis-8-hydroxyquinolinatocopper(II) molecules and isolated picryl azide molecules in the ratio 1 : 2. In the unit cell of the crystal, these molecules occupy four distinct planes parallel to the ab plane at heights z/c of approximately 1/12,

[1] D. W. J. Cruickshank and F. R. Ahmed, *Acta Cryst.*, 1953, **6**, 385.
[2] S. F. Darlow, *Acta Cryst.*, 1960, **13**, 683.

TABLE 1

Observed structure amplitudes and calculated structure factors for (*hkl*)

h	*k*	*l*	$5\|F_o\|$	$5F_c$	*h*	*k*	*l*	$5\|F_o\|$	$5F_c$	*h*	*k*	*l*	$5\|F_o\|$	$5F_c$
0	4	4	39	42			−2	162	176	2	−34	0	64	−60
0	5	1	277	−275	1	−17	−3	172	118	2	−33	−1	61	−67
		3	93	80	1	−15	−1	43	57	2	−31	−1	72	−76
0	6	0	240	284	1	−14	−4	120	110	2	−30	0	125	−118
		2	113	−101			−2	179	156	2	−27	−1	44	−24
		4	66	−86	1	−13	−1	126	−115	2	−26	−2	34	−53
0	7	1	186	170	1	−12	−4	50	43	2	−25	−1	85	−111
		3	88	88			−2	293	305	2	−24	−2	53	−51
0	8	0	176	184	1	−11	−3	84	66			0	175	−172
		2	242	247			−1	133	−115	2	−23	−1	87	−76
0	9	1	356	−324	1	−10	−2	177	164	2	−22	0	112	−87
		3	156	−142	1	−9	−1	57	38	2	−20	−2	30	−31
0	10	0	248	216	1	−8	−4	57	59			0	176	−183
0	11	1	93	93			−2	225	208	2	−19	−1	147	−148
		3	108	67	1	−7	−3	23	15	2	−18	0	177	−172
0	12	0	107	83			−1	247	−267	2	−17	−1	86	65
		2	80	76	1	−6	−4	31	54	2	−16	−4	53	55
		4	41	−43			−2	383	446			−2	118	−97
0	13	1	44	−48	1	−5	−3	72	81			0	229	−226
		3	118	−108			−1	75	61	2	−15	−1	112	94
0	14	0	41	−1	1	−4	−4	72	−81	2	−14	−4	74	61
		2	121	112	1	4	2	228	258			−2	120	−101
0	15	1	221	183			4	43	43			0	483	−563
0	16	0	97	82	1	5	1	95	−111	2	−13	−1	97	−80
0	17	1	194	172			3	32	−15	2	−12	−4	171	175
		3	74	−61	1	6	2	149	−148			−2	75	−66
0	18	0	158	124			4	91	−107			0	360	−403
		2	164	153	1	7	1	154	−163	2	−11	−1	209	−286
0	19	1	94	86			3	93	−61	2	−10	−4	45	50
0	21	1	168	170	1	8	2	80	70			−2	74	62
0	22	0	259	237	1	10	2	44	−30			0	70	−57
		2	135	134			4	125	−112	2	−9	−1	92	85
0	23	1	179	174	1	11	1	195	−223	2	−8	−4	40	41
0	24	0	312	341			3	90	−70			−2	160	−178
		2	131	127	1	12	2	31	30			0	563	−658
		4	118	−111	1	13	3	57	−39	2	−7	−3	77	66
0	25	1	112	115	1	14	2	125	−102			−1	81	−77
0	26	0	107	94			4	82	−85	2	−6	−4	82	115
0	28	0	56	51	1	15	1	166	−147			−2	109	−103
0	30	0	86	85			3	111	−100			0	197	−213
0	32	0	51	44	1	16	4	50	−38	2	−5	−1	179	−133
0	36	0	133	113	1	17	1	116	−112	2	−4	−4	107	124
		2	43	35			3	116	−103			−2	143	122
1	−38	−2	24	46	1	18	2	147	−134			0	268	−328
1	−37	−1	61	−2			4	47	−53	2	−2	−4	49	132
1	−36	−2	34	66	1	19	3	108	−100	2	0	4	34	−33
1	−31	−1	46	54	1	20	2	73	−70	2	2	0	279	339
1	−30	−2	58	73	1	21	1	176	−174			4	97	−115
1	−28	−2	67	75			3	168	−183	2	3	1	111	−104
1	−26	−2	74	51	1	22	2	286	−372			3	147	177
1	−25	−1	126	140			4	156	−165	2	4	0	241	245
1	−24	−4	91	101	1	23	3	103	−96			2	166	−145
		−2	103	118	1	24	2	279	−269	2	5	1	607	−624
1	−23	−3	117	101			4	91	−91	2	6	0	29	40
		−1	32	46	1	26	2	60	53			2	112	102
1	−22	−4	67	75			4	64	52			4	44	22
		−2	113	100	1	30	2	56	−54	2	7	1	151	160
1	−21	−3	98	89	1	34	2	33	−52	2	8	0	118	−106
		−1	91	85	1	36	2	31	−29			2	156	−152
1	−19	−3	113	96	2	−38	0	69	−56			4	29	−28
		−1	135	138	2	−37	−1	51	−71	2	9	1	246	−259
1	−18	−4	57	85	2	−35	−1	43	−50			3	76	56

TABLE 1 (*Continued*)

h	*k*	*l*	$5\|F_o\|$	$5F_c$
2	10	0	57	94
		2	111	−71
		4	32	39
2	11	1	43	40
		3	41	20
2	12	0	454	−507
		2	95	−99
		4	44	31
2	13	1	56	−62
2	14	0	131	129
		2	55	54
		4	85	76
2	15	1	164	−166
2	16	0	297	−327
		2	101	−88
2	17	1	92	−84
2	18	0	148	−127
		2	70	58
		4	76	70
2	19	1	174	−201
2	20	0	294	−310
		2	133	−129
		4	88	82
2	21	1	87	−80
		3	52	42
2	22	0	457	−528
		2	163	−152
		4	112	121
2	23	3	71	−60
2	24	0	93	−61
2	26	0	187	167
		2	54	60
		4	51	−40
2	34	0	59	−42
		2	31	−37
2	36	0	34	−12
3	−37	−1	45	−50
3	−36	−2	54	−46
3	−30	−2	89	−82
3	−27	−3	65	−47
3	−26	−2	86	−75
3	−24	−2	89	−120
3	−23	−3	75	−67
3	−22	−2	112	−115
3	−21	−3	77	−71
3	−20	−2	97	−95
3	−19	−3	95	−81
		−1	61	−77
3	−17	−1	92	66
3	−16	−4	113	−110
		−2	343	−333
3	−15	−1	42	31
3	−14	−4	156	−155
		−2	346	−308
3	−13	−3	331	−341
		−1	375	−427
3	−12	−4	41	−73
		−2	142	−138
3	−11	−3	110	−113
3	−10	−2	91	−83
3	−9	−3	167	−175
		−1	271	−314
3	−8	−4	54	−79
		−2	38	24
3	−7	−1	165	−152
3	−6	−4	64	−87
		−2	199	−217
3	−5	−3	109	−98
		−1	87	86
3	−4	−4	23	−13
		−2	121	137
3	−3	−3	46	−49
		−1	297	−314
3	−2	−4	148	−182
		−2	57	60
3	−1	−3	242	−304
		−1	243	−271
3	0	2	52	−50
3	1	1	114	100
		3	91	97
3	2	2	146	163
		4	89	95
3	3	1	380	386
		3	180	182
3	4	2	48	−53
3	5	3	206	221
3	6	2	91	82
		4	33	44
3	7	3	74	−53
3	8	2	193	175
		4	113	93
3	9	1	103	90
		3	182	185
3	10	2	269	285
		4	83	78
3	11	3	167	152
3	12	2	185	189
3	13	1	74	64
		3	42	45
3	14	2	84	84
3	15	1	44	37
		3	147	123
3	16	2	179	195
		4	78	77
3	17	1	58	61
		3	66	76
3	18	2	67	61
3	19	1	102	105
		3	152	165
3	20	2	186	218
		4	97	92
3	21	1	33	−33
3	22	2	169	141
		4	110	114
3	23	1	59	64
		3	77	63
3	24	2	132	−124
3	25	1	56	42
		3	70	61
3	27	1	68	76
		3	60	58
4	−38	0	67	39
4	−37	−1	37	51
4	−36	0	86	78
4	−35	−1	39	58
4	−33	−1	31	16
4	−32	−2	39	43
		0	104	107
4	−31	−1	91	82
4	−29	−1	69	74
4	−28	0	114	104
4	−26	0	87	92
4	−24	−2	46	55
		0	86	78
4	−23	−1	52	50
4	−22	0	104	97
4	−21	−3	61	30
		−1	98	92
4	−20	−2	70	64
		0	47	−39
4	−19	−1	149	157
4	−18	−4	51	−42
		0	100	90
4	−16	−4	118	−95
		−2	226	214
		0	504	511
4	−15	−3	148	−131
		−1	298	318
4	−14	−2	223	200
		0	190	168
4	−13	−1	453	524
4	−12	−4	63	−59
		−2	81	−58
4	−11	−1	149	144
4	−10	−2	108	84
		0	144	−125
4	−9	−3	48	−51
		−1	259	310
4	−8	0	84	−112
4	−7	−3	37	−15
4	−6	−4	27	30
		−2	178	200
		0	327	314
4	−5	−3	53	−51
		−1	167	−130
4	−4	−4	40	−34
		−2	121	−138
		0	489	−543
4	−3	−1	460	513
4	−2	−4	50	58
		0	171	146
4	−1	−1	212	183
4	0	0	161	136
		4	108	−124
4	1	1	402	425
		3	102	109
4	2	0	422	461
		2	116	89
		4	42	−45
4	3	1	47	−55
		3	73	−54
4	4	0	88	77
		4	36	25
4	5	1	344	379
		3	108	106
4	6	0	106	97

TABLE 1 (*Continued*)

h	*k*	*l*	5|F_o|	5F_c
		2	44	50
		4	98	−88
4	7	1	76	−59
		3	39	18
4	8	0	740	800
		2	131	127
		4	137	−126
4	9	1	450	473
		3	64	65
4	10	0	132	136
		4	107	−121
4	11	1	178	160
		3	92	−57
4	12	0	94	111
4	14	0	94	116
4	15	1	76	83
		3	64	−49
4	16	2	97	86
4	17	1	181	185
4	18	2	74	−68
4	19	1	57	26
4	20	0	175	153
		2	120	130
4	21	1	60	85
4	22	0	61	−35
		2	60	45
4	23	1	183	165
4	25	1	113	123
4	27	1	100	97
4	30	0	48	57
4	31	1	49	50
4	32	0	37	44
4	34	0	37	61
5	−37	−1	33	44
5	−34	−2	28	70
5	−32	−2	31	32
5	−31	−3	92	96
		−1	84	87
5	−29	−3	81	94
		−1	61	72
5	−28	−2	90	98
5	−25	−3	77	81
		−1	60	76
5	−22	−4	72	53
		−2	75	77
5	−21	−3	102	115
		−1	125	115
5	−19	−3	59	79
		−1	51	52
5	−18	−4	68	92
		−2	144	129
5	−17	−3	142	120
		−1	150	181
5	−16	−4	87	70
		−2	134	111
5	−15	−3	252	266
		−1	195	201
5	−14	−4	122	121
		−2	131	139
5	−13	−3	154	165
		−1	133	142
5	−12	−4	49	54
		−2	54	63
5	−11	−3	72	110
		−1	114	135
5	−10	−2	64	45
5	−9	−3	186	170
5	−8	−4	77	69
		−2	107	79
5	−7	−3	105	109
		−1	178	176
5	−5	−3	144	119
		−1	80	62
5	−4	−2	176	151
5	−3	−3	64	88
5	−1	−3	159	184
		−1	213	268
5	0	2	232	−209
		4	65	−48
5	1	1	143	152
		3	108	−94
5	2	2	123	−143
		4	47	−30
5	3	1	232	−235
		3	183	−223
5	4	4	60	−73
5	5	1	125	−129
		3	95	−96
5	6	2	338	−378
		4	101	−93
5	7	1	99	−92
		3	196	−218
5	8	2	321	−339
		4	152	−152
5	9	1	302	−319
		3	188	−208
5	10	2	76	60
5	11	1	138	−134
		3	188	−192
5	12	2	60	34
5	13	3	58	30
5	14	4	83	−69
5	15	1	133	−132
		3	96	−78
5	17	3	63	−67
5	19	1	59	−64
5	21	1	112	−112
5	23	1	75	−90
		3	366	−110
5	25	1	91	−62
		3	95	−61
5	27	3	70	−55
5	29	3	33	−27
6	−36	0	62	−73
6	−35	−1	49	−65
6	−34	0	48	−53
6	−33	−1	55	−59
6	−32	0	98	−72
6	−31	−1	151	−182
6	−28	0	93	−90
6	−25	−1	60	−78
6	−23	−1	65	−66
6	−22	−4	61	64
		0	203	−159
6	−21	−1	84	−82
6	−19	−1	154	−162
6	−17	−1	182	−188
6	−16	0	192	−210
6	−15	−1	200	−223
6	−14	−4	63	58
		−2	160	−184
		0	274	−302
6	−13	−1	139	−161
6	−12	0	129	−150
6	−11	−3	75	−49
		−1	279	−251
6	−10	−4	89	72
		−2	58	69
		0	204	−206
6	−9	−1	219	−238
6	−8	−4	53	50
		−2	84	−61
		0	94	91
6	−7	−3	99	80
		−1	446	−515
6	−6	−2	69	69
		0	199	−165
6	−5	−3	51	39
		−1	216	224
6	−4	−4	70	56
		−2	140	−106
		0	278	−270
6	−3	−3	54	43
		−1	44	30
6	−2	−2	45	41
		0	372	336
6	−1	−3	78	−75
		−1	283	−351
6	0	0	206	−163
		2	30	38
		4	50	51
6	1	1	168	−111
6	2	0	139	−115
		2	144	−147
		4	67	63
6	3	1	328	−398
		3	65	36
6	4	0	180	−175
		2	32	−37
		4	39	46
6	5	1	75	−92
		3	99	81
6	6	0	531	−609
		2	231	−255
		4	81	77
6	7	1	270	−316
6	8	0	142	130
		2	26	−17
		4	54	44
6	9	1	347	−385
6	10	4	62	−43
6	11	1	55	−60
6	12	0	162	121
6	13	1	85	−88
6	14	0	170	−164
		2	90	−80

TABLE 1 (*Continued*)

h	k	l	$5\|F_o\|$	$5F_c$
6	15	3	63	43
6	17	1	123	−146
6	21	1	172	−182
6	22	0	69	−84
6	24	0	156	−153
6	25	1	83	−69
6	26	2	43	6
6	28	0	76	−95
6	29	1	73	−58
6	30	0	84	−109
6	32	0	57	−62
7	−35	−3	30	−26
7	−33	−3	85	−93
		−1	55	−50
7	−32	−2	76	−77
7	−31	−3	63	−82
		−1	53	−78
7	−28	−2	60	−56
7	−25	−3	92	−88
		−1	80	−102
7	−24	−2	67	−69
7	−23	−3	58	−49
7	−22	−2	97	−99
7	−21	−3	75	−77
		−1	31	−34
7	−19	−3	100	−110
		−1	94	−90
7	−17	−3	124	−122
7	−16	−4	63	−80
7	−15	−3	142	−125
		−1	116	−137
7	−14	−4	83	−96
		−2	136	−151
7	−13	−3	154	−197
		−1	127	−138
7	−12	−4	80	−78
		−2	168	−178
7	−11	−3	93	−94
		−1	109	−107
7	−10	−4	51	−52
		−2	102	−92
7	−9	−3	266	−302
		−1	349	−330
7	−7	−3	197	−202
		−1	186	−171
7	−6	−4	65	−44
		−2	50	−48
7	−5	−3	260	230
		−1	107	111
7	−4	−4	73	−55
		−2	67	−50
7	−3	−1	39	56
7	−2	−2	121	111
7	−1	−3	146	−170
		−1	208	−208
7	0	2	133	146
		4	6	91
7	1	1	163	152
		3	88	74
7	2	2	134	142
		4	36	29
7	3	1	112	86
		3	207	198
7	4	2	156	171
		4	102	116
7	5	1	143	143
		3	47	50
7	6	2	74	77
		4	60	72
7	7	1	124	127
		3	209	213
7	8	2	65	61
		4	46	68
7	9	1	71	53
		3	111	109
7	10	2	74	71
		4	59	70
7	11	1	96	110
		3	66	62
7	12	2	72	80
7	13	3	99	119
7	14	2	101	87
7	15	1	58	60
7	16	2	53	58
7	17	1	54	71
		3	53	59
7	19	3	32	34
7	21	1	62	51
		3	31	48
7	22	2	42	69
7	23	3	65	54
7	24	2	50	96
7	26	2	89	49
7	27	1	46	49
7	30	2	61	48
8	−38	0	74	62
8	−37	−1	31	38
8	−35	−1	27	55
8	−34	0	119	104
8	−33	−1	82	40
8	−30	0	91	96
8	−29	−1	80	−52
8	−28	0	49	55
8	−27	−1	62	89
8	−26	0	82	88
8	−23	−1	123	136
8	−21	−1	84	65
8	−20	−2	51	48
		0	81	75
8	−19	−1	157	142
8	−18	−4	85	−77
		0	76	77
8	−17	−1	98	91
8	−16	−4	53	−48
		−2	83	83
		0	164	180
8	−15	−1	232	250
8	−14	−2	83	53
		0	206	207
8	−13	−3	88	−83
		−1	144	140
8	−12	−2	156	226
		0	227	218
8	−11	−3	68	−56
		−1	131	137
8	−10	−4	59	−75
		−2	26	−35
		0	108	103
8	−9	−3	79	52
		−1	446	460
8	−8	−2	25	47
		0	78	32
8	−7	−3	61	−60
		−1	73	−53
8	−6	−4	57	−46
		−2	132	114
		0	100	87
8	−5	−3	68	72
		−1	298	−262
8	−4	−2	25	−34
		0	121	131
8	−3	−3	68	−55
8	−2	−4	50	−55
		−2	155	126
		0	208	152
8	−1	0	208	152
8	−1	−1	248	260
8	0	0	39	38
		2	50	−62
		4	58	−66
8	1	1	114	109
		3	58	43
8	2	0	352	344
		2	69	69
		4	49	−53
8	3	1	92	88
8	4	2	85	72
8	5	1	179	182
		3	45	−40
8	6	0	228	235
		2	56	68
		4	41	30
8	7	1	84	77
8	8	0	246	266
		2	92	89
		4	75	−86
8	9	1	171	170
8	10	0	161	173
		2	49	53
		4	43	−56
8	11	1	146	143
8	12	0	112	117
		2	32	−19
8	13	1	71	73
8	14	0	108	99
		2	83	85
8	16	0	74	84
8	18	0	69	79
8	21	1	86	80
8	22	0	110	125
8	23	1	58	56
8	24	0	93	84
8	25	1	48	54
8	26	0	102	103
8	28	0	81	62

TABLE 1 (*Continued*)

h	*k*	*l*	5|F_o|	5F_c
9	−33	−3	34	46
9	−28	−2	72	76
9	−27	−3	69	82
9	−25	−1	34	60
9	−23	−3	153	130
		−1	122	138
9	−21	−3	133	119
		−1	87	83
9	−20	−4	121	137
		−2	204	261
9	−19	−3	70	−51
		−1	69	59
9	−17	−3	92	100
		−1	61	43
9	−16	−2	78	85
9	−15	−3	60	65
		−1	52	32
9	−14	−4	75	86
		−2	93	103
9	−13	−3	85	74
		−1	145	134
9	−12	−4	87	80
		−2	103	124
9	−11	−3	94	104
9	−10	−2	148	167
9	−9	−3	131	119
		−1	110	93
9	−8	−4	56	58
		−2	98	99
9	−7	−3	100	−71
		−1	111	−74
9	−6	−4	50	52
		−2	130	136
9	−5	−1	132	−119
9	−4	−2	155	162
9	−3	−3	147	110
		−1	181	131
9	−2	−4	50	44
		−2	120	117
9	−1	−3	141	120
9	0	2	77	−77
9	1	1	44	−39
		3	82	−87
9	2	2	118	−132
		4	63	−99
9	3	1	79	−81
		3	79	−84
9	4	2	87	−79
9	5	1	118	−104
		3	171	−151
9	6	2	79	−101
9	7	1	43	−55
9	8	2	213	−265
		4	86	−102
9	9	1	56	−62
		3	143	−149
9	10	2	52	−68
9	11	1	77	−70
		3	81	−68
9	12	2	98	−106
		4	61	−74
9	13	3	46	−63
9	15	3	77	−62
9	16	2	68	−61
9	17	3	114	117
9	18	2	54	−49
9	20	2	32	−61
9	22	2	60	−74
9	23	1	43	−57
		3	45	−49
9	24	2	38	−52
9	26	2	50	−64
10	−34	0	44	−57
10	−33	−1	46	−45
10	−30	−2	61	−66
		0	58	−83
10	−29	−1	66	−87
10	−28	0	55	−93
10	−26	−2	85	−75
		0	111	−101
10	−25	−1	109	−111
10	−24	0	105	97
10	−23	−3	46	18
		−1	198	−244
10	−22	−4	71	79
		−2	112	−109
		0	299	−346
10	−21	−1	60	32
10	−20	−4	82	105
		−2	107	−115
		0	247	−295
10	−19	−3	41	−4
		−1	98	114
10	−18	−2	65	56
		0	87	64
10	−17	−3	40	−38
10	−15	−1	89	−84
10	−14	−2	97	−72
		0	241	−228
10	−12	−2	38	−52
		0	175	−201
10	−11	−3	48	−42
10	−10	−4	75	71
		−2	118	−123
		0	267	−305
10	−9	−3	59	−30
		−1	90	−68
10	−8	0	214	−213
10	−7	−1	89	−77
10	−6	−4	83	72
		−2	83	−74
		0	231	−190
10	−5	−1	76	−64
10	−4	−4	41	53
		−2	76	−73
		0	241	−216
10	−3	−1	152	−136
10	−2	0	175	−118
10	−1	−3	65	59
		−1	83	−72
10	0	0	65	−39
		2	93	−107
10	1	1	156	−195
10	2	0	213	−199
		4	60	70
10	3	1	98	−108
10	4	0	126	−151
		2	43	−67
10	5	3	50	54
10	6	0	62	−72
10	7	1	83	−86
		3	64	−47
10	8	0	277	−268
		2	92	−93
10	10	0	128	−106
		2	94	−100
10	11	1	111	−135
10	12	0	48	−59
10	13	1	61	−79
10	14	0	107	−110
10	16	0	99	−99
		2	54	−67
10	17	1	86	106
10	18	0	116	−124
10	19	1	59	−96
10	20	0	46	−46
10	21	1	43	−86
10	22	0	54	−64
10	24	0	34	−51
10	26	0	82	−76
11	−32	−2	58	−84
11	−31	−3	44	−58
11	−29	−3	49	−73
		−1	64	−53
11	−28	−2	114	−118
11	−26	−2	72	−69
11	−25	−3	128	−136
		−1	87	−90
11	−24	−2	80	−88
11	−23	−3	95	−98
		−1	75	−80
11	−22	−4	86	−112
		−2	199	−267
11	−21	−3	99	94
		−1	113	111
11	−20	−2	47	−61
11	−19	−3	82	82
		−1	110	87
11	−18	−4	61	64
		−2	110	110
11	−15	−3	90	−112
11	−14	−2	96	−99
11	−12	−4	67	−85
		−2	83	−104
11	−11	−3	94	−124
		−1	73	−80
11	−10	−2	166	−149
11	−7	−3	92	−86
		−1	181	−144
11	−6	−4	54	−67
		−2	90	−78
11	−5	−3	156	−155
		−1	71	−85
11	−4	−4	72	−74
		−2	164	−148
11	−3	−3	92	−107

TABLE 1 (*Continued*)

h	*k*	*l*	5|F_o|	5F_c
		−1	72	−71
11	−1	−3	188	−184
		−1	196	−204
11	0	2	103	96
11	1	1	62	83
		3	129	142
11	2	2	187	207
		4	82	95
11	3	3	112	−129
11	7	3	77	90
11	8	2	105	110
		4	72	80
11	10	2	101	112
11	11	3	58	75
11	13	3	45	60
11	14	2	89	102
11	16	2	52	76
11	18	2	30	56
12	−36	0	62	37
12	−34	0	109	100
12	−32	0	87	83
12	−30	0	97	89
12	−29	−1	68	102
12	−28	−4	50	−40
		0	148	148
12	−26	0	135	141
12	−25	−1	124	138
12	−24	−4	59	−70
		0	105	107
12	−22	−2	85	85
		0	253	246
12	−21	−1	108	−115
12	−20	−2	68	−79
		0	130	−145
12	−19	−1	68	−57
12	−17	−1	101	108
12	−16	0	60	82
12	−15	−1	123	155
12	−14	−2	78	97
		0	116	84
12	−13	−3	52	−45
		−1	53	47
12	−12	0	104	78
12	−11	−1	175	185
12	−10	−2	125	123
		0	246	253
12	−9	−3	76	−52
		−1	84	60
12	−8	−2	117	121
		0	219	189
12	−7	−1	242	221
12	−6	0	64	99
12	−5	−1	163	149
12	−4	−4	61	−64
		−2	117	106
		0	219	193
12	−3	−1	126	118
12	−1	−3	64	−49
		−1	281	222
12	0	0	265	253
		2	119	114
12	1	1	155	−172
12	2	0	251	204
		2	103	92
		4	61	−73
12	3	1	167	−190
		3	77	76
12	4	0	201	−132
		2	111	−120
12	7	1	113	127
12	8	0	207	218
		2	80	90
12	10	0	173	182
		2	42	48
12	12	0	69	75
12	13	1	48	92
12	14	0	114	127
12	15	1	46	43
12	16	0	58	72
12	18	0	38	44
13	−30	−2	33	45
13	−29	−3	53	66
13	−28	−2	63	76
13	−26	−2	62	69
13	−24	−2	46	68
13	−23	−3	49	47
13	−17	−3	82	78
		−1	87	80
13	−15	−3	52	53
		−1	68	62
13	−14	−2	48	27
13	−13	−3	71	84
		−1	61	69
13	−12	−2	85	98
13	−11	−3	77	75
		−1	111	121
13	−10	−2	171	162
13	−9	−3	77	69
13	−8	−2	105	109
13	−7	−3	126	131
		−1	100	110
13	−6	−4	61	73
		−2	111	114
13	−5	−1	79	99
13	−4	−2	158	121
13	−3	−3	146	135
13	0	2	142	−149
		4	81	−90
13	1	1	155	165
		3	189	184
13	3	1	99	94
		3	52	46
13	4	2	112	118
13	5	1	128	−123
		3	125	−108
13	6	2	95	−72
13	7	1	56	−66
		3	115	−117
13	8	2	104	−113
13	9	3	49	−60
13	10	2	71	−84
13	11	3	49	−70
13	12	2	50	−65
13	13	3	78	−100
13	14	2	37	−53
13	17	3	48	−73
14	−28	0	70	−71
14	−26	0	56	−56
14	−25	−1	80	−97
14	−23	−1	78	−82
14	−21	−1	67	−83
14	−20	0	61	−39
14	−17	−1	87	−99
14	−16	−2	34	−9
14	−14	0	134	−136
14	−13	−1	103	−107
14	−12	0	139	−139
14	−10	0	183	−163
14	−9	−1	120	−96
14	−8	0	92	−73
14	−7	−1	103	−79
14	−6	−2	106	−107
		0	188	−205
14	−5	−1	55	−96
14	−4	−2	85	64
14	−3	−3	77	−51
		−1	103	−103
14	−2	−2	60	−58
		0	105	−90
14	−1	−1	109	90
14	0	0	179	−129
		2	74	−42
14	3	3	63	46
14	5	1	182	−205
14	7	1	125	−93
14	8	0	89	−100
		2	70	−77
14	10	0	92	−77
		2	30	−35
14	11	1	99	−103
14	12	0	91	−95
		2	36	−47
14	13	1	53	−67
14	15	1	38	−77
15	−29	−3	43	−13
15	−27	−3	35	−54
15	−25	−3	62	−63
		−1	53	−65
15	−23	−1	69	−68
15	−22	−2	54	−39
15	−20	−2	56	−63
15	−15	−3	67	−36
15	−14	−2	131	−148
15	−13	−3	44	−13
15	−12	−2	60	−51
15	−7	−3	80	−77
15	−6	−2	79	−61
15	−5	−3	63	−60
15	−3	−3	44	−25
15	−2	−2	100	−89
15	−1	−3	44	−32
15	1	1	124	111
		3	96	79
15	3	3	53	77
15	5	1	77	67
		3	90	93

TABLE 1 (*Continued*)

h	*k*	*l*	$5\|F_o\|$	$5F_c$	*h*	*k*	*l*	$5\|F_o\|$	$5F_c$	*h*	*k*	*l*	$5\|F_o\|$	$5F_c$
15	6	2	61	17	16	0	0	117	115	16	−3	−1	89	91
15	7	3	43	41	16	−17	−1	71	91	16	−2	0	60	77
15	8	2	58	61	16	−16	0	100	114	16	−1	−1	129	137
15	9	3	50	72	16	−12	0	120	−119	16	1	1	81	101
15	10	2	44	51	16	−10	0	86	−54	16	2	0	76	59
15	11	3	45	43	16	−7	−1	79	75	16	8	0	80	65
16	−26	0	64	70	16	−6	−2	86	80	16	10	0	74	71
16	−24	−2	57	57			0	68	78	17	−26	−2	54	58
16	−23	−1	52	81	16	−5	−1	79	85	17	−24	−2	32	43
16	−22	0	54	40	16	−4	0	60	66	17	−22	−2	55	74
										17	1	3	48	−63

TABLE 2

Atomic co-ordinates (× 10^4) and standard deviations (× 10^4)

	x/a	$\sigma(x/a)$	*y/b*	$\sigma(y/b)$	*z/c*	$\sigma(z/c)$
Cu	2500	0	0	0	878	5
C(1)	2661	7	899	3	811	21
C(2)	2529	7	1326	4	739	27
C(3)	3224	7	1720	3	740	22
C(4)	4081	6	1699	3	948	26
C(5)	4218	7	1275	4	913	23
C(6)	5049	6	1195	3	1104	24
C(7)	5143	7	768	4	1193	24
C(8)	4394	6	389	3	1041	22
C(9)	3508	5	883	3	878	20
M(1)	3621	4	447	2	927	17
O(1)	2018	3	514	2	740	15
C(10)	8220	6	874	3	4228	24
C(11)	9040	5	799	3	4038	22
C(12)	9778	5	1145	3	3930	23
C(13)	9687	6	1579	3	4127	25
C(14)	8903	6	1679	3	4299	24
C(15)	8194	5	1321	3	4328	23
N(2)	9084	5	335	3	3802	20
N(3)	536	5	1941	3	4165	20
N(4)	8999	6	2157	3	4265	20
N(5)	8450	6	2309	3	5078	18
N(6)	8036	8	2513	3	5696	25
N(7)	7299	6	1382	3	4264	21
O(2)	8461	5	35	3	4116	20
O(3)	9782	6	273	3	3455	18
O(4)	5664	5	2182	3	4515	19
O(5)	988	5	1943	3	2757	18
O(6)	7191	5	1723	3	3703	19
O(7)	6707	5	1067	3	4714	22

5/12, 7/12, and 11/12. Each plane contains metal complexes and picryl azide molecules also in the ratio 1 : 2 (Figure 1). The resulting arrangement is such that metal complexes alternate with pairs of picryl azide molecules in stacks perpendicular to the *ab* plane. The periodicity of the stack is the crystallographic *c*-spacing and the picryl azide molecules are approximately mid-way between the metal complexes. The crystal has therefore a structure characteristic of a " polarisation bonded " or " charge-transfer " adduct. There is no co-ordinate linkage between the copper atom and the picryl azide molecule.

In this crystal, in which the crystallographic diad axis passes through the copper atom, bis-8-hydroxyquinolinatocopper(II) has the shape of a two-bladed propeller of small pitch. Each 8-hydroxyquinoline residue is itself planar within experimental error, the deviation of any atom from the best plane not exceeding twice the standard deviation of its *z*-co-ordinate. The mean and maximum deviations are 0·02 and 0·036 Å, respectively. There are no anomalous interatomic distances within the residue (Figure 3). The angle between

TABLE 3

Thermal parameters ($\times 10^4$). The temperature factor, T, is equal to $2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)}$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cu	34	10	545	0	0	9
C(1)	78	13	337	−5	−86	3
C(2)	55	17	729	8	75	33
C(3)	69	14	372	38	29	23
C(4)	54	11	782	36	−16	13
C(5)	66	17	451	−2	−11	27
C(6)	51	11	683	−55	48	7
C(7)	46	18	688	23	47	11
C(8)	34	12	479	−21	−30	5
C(9)	27	18	385	5	78	10
N(1)	24	13	439	5	−53	5
O(1)	22	13	651	39	−14	23
C(10)	30	17	643	−6	51	9
C(11)	25	13	593	13	47	18
C(12)	13	15	637	5	7	8
C(13)	35	16	688	47	112	3
C(14)	31	12	728	−12	24	16
C(15)	19	15	586	4	−15	5
N(2)	40	13	804	−16	−8	−5
N(3)	47	15	641	27	36	11
N(4)	69	14	603	22	24	17
N(5)	60	13	547	−18	−2	27
N6	134	18	826	19	67	39
N7	62	20	613	20	60	25
O(2)	76	19	1009	−12	−6	19
O(3)	91	18	865	−16	69	36
O(4)	74	21	812	40	75	−1
O(5)	58	21	783	44	147	10
O(6)	74	22	1001	−3	53	47
O(7)	49	27	1228	9	39	10

TABLE 4

Atomic co-ordinates (in Å) referred to the orthogonal axes a,b^*,c

	X'	Y'	Z'		X'	Y'	Z'
Cu	2·950	0·000	0·606	C(13)	11·430	4·709	2·848
C(1)	3·140	2·681	0·560	C(14)	10·505	5·007	2·966
C(2)	2·984	3·954	0·510	C(15)	9·669	3·939	2·986
C(3)	3·804	5·129	0·511	N(2)	11·939	0·999	2·623
C(4)	4·977	5·066	0·654	N(3)	0·632	5·788	2·874
C(5)	5·992	3·802	0·630	N(4)	10·619	6·432	2·943
C(6)	5·958	3·563	0·762	N(5)	9·971	6·885	3·504
C(7)	6·069	2·290	0·823	N(6)	9·482	7·494	3·930
C(8)	5·185	1·150	0·718	N(7)	8·613	4·121	2·942
C(9)	4·125	2·633	0·606	O(2)	9·984	0·104	2·840
O(1)	4·273	1·333	0·640	O(3)	11·543	0·814	2·384
N(1)	2·381	1·533	0·511	O(4)	6·683	6·507	3·115
C(10)	9·700	2·606	2·917	O(5)	1·166	5·794	1·902
C(11)	10·667	2·383	2·786	O(6)	8·485	5·138	2·555
C(12)	11·538	3·414	2·712	O(7)	7·914	3·182	3·253

the least-squares best planes of the pair of 8-hydroxyquinoline residue in any one copper complex is approximately 7°. The copper–nitrogen bonds are equal in length to the copper–oxygen bonds within the limits of error of the determination.

The nearest atoms to the copper atom, other than those within the bis-8-hydroxyquinolinate-complex are two pairs of oxygen atoms O(2) of four different picryl azide molecules at 3·77 and 3·78 Å. Neither pair of oxygen atoms completes an octahedral co-ordination sphere about the copper atom. It is, therefore, truly four-co-ordinate and nearly planar (Figure 4).

The propeller-shaped complex is sensibly different from the bow-shaped molecule

TABLE 5

Inter-atomic distances with standard deviations in parentheses

(*a*) *The* bis-8-*hydroxyquinolinatocopper*(II) *molecule*

Cu–N(1)	1·96(0·01)	C(4)–C(5)	1·39(0·02)
Cu–O(1)	1·95(0·01)	C(5)–C(6)	1·44(0·02)
C(1)–C(2)	1·40(0·02)	C(5)–C(9)	1·43(0·02)
C(1)–O(1)	1·35(0·02)	C(6)–C(7)	1·37(0·02)
C(1)–C(9)	1·38(0·02)	C(7)–C(8)	1·44(0·02)
C(2)–C(3)	1·42(0·02)	C(8)–N(1)	1·31(0·01)
C(3)–C(4)	1·41(0·02)	C(9)–N(1)	1·38(0·02)

(*b*) *The picryl azide molecule*

C(10)–C(11)	1·41(0·02)	N(2)–O(2)	1·19(0·02)
C(10)–C(15)	1·39(0·02)	N(2)–O(3)	1·22(0·02)
C(11)–C(12)	1·37(0·02)	N(3)–O(4)	1·16(0·02)
C(11)–N(2)	1·47(0·02)	N(3)–O(5)	1·21(0·02)
C(12)–C(13)	1·39(0·02)	N(4)–N(5)	1·24(0·02)
C(13)–C(14)	1·39(0·02)	N(5)–N(6)	1·12(0·02)
C(13)–N(3)	1·52(0·02)	N(7)–O(6)	1·18(0·02)
C(14)–C(15)	1·36(0·02)	N(7)–O(7)	1·21(0·02)
C(14)–N(4)	1·46(0·02)	N(5) · · · O(6)	2·52
C(15)–N(7)	1·51(0·02)	N(5) · · · O(5)	2·98
		N(6) · · · O(6)	2·82
		N(6) · · · O(5)	3·09

(*c*) *Between* bis-8-*hydroxyquinolinatocopper*(II) *and picryl azide molecules*

C(2) · · · N(7)	3·48	C(6) · · · C(12)	3·45
C(2) · · · N(7)′	3·48	C(6) · · · C(12)	3·50
C(2) · · · O(6)	3·34	C(7) · · · O(7)	3·45
C(2) · · · O(7)	3·42	C(8) · · · N(2)	3·38
C(3) · · · N(5)	3·38	C(8) · · · O(3)	3·20
C(3) · · · O(4)	3·39	C(8) · · · O(3)	3·19
C(3) · · · O(6)	3·49	C(9) · · · C(10)	3·41
C(4) · · · C(14)	3·29		

All other contacts between molecules are longer than these

Cu · · · O(2)	3·78	Cu · · · O(2)	3·77

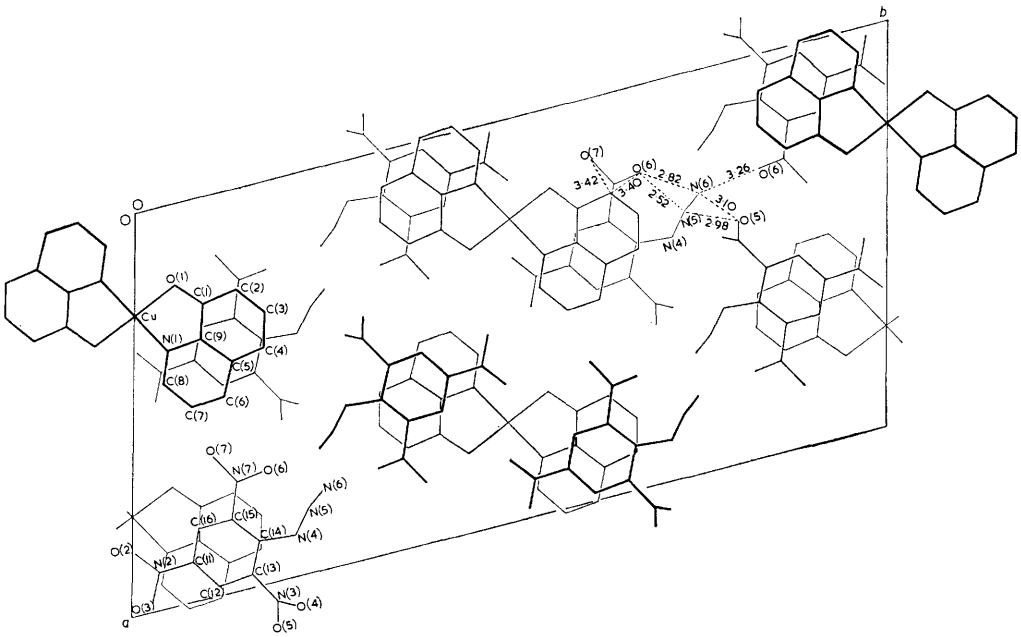


FIGURE 2. The crystal structure projected down the *c* axis, showing the relative arrangement of atoms in donor and acceptor molecules

observed in the five-co-ordinate dimeric form of bis-8-hydroxyquinolinatocopper(II) itself [3] or the planar molecule in the bis-8-hydroxyquinolinatocopper(II)–benzotrifuroxan adduct.[4] This is probably indicative of no more than the flexible nature of this co-ordination complex. Figure 5 shows the picryl azide molecule projected on to, and perpendicular to,

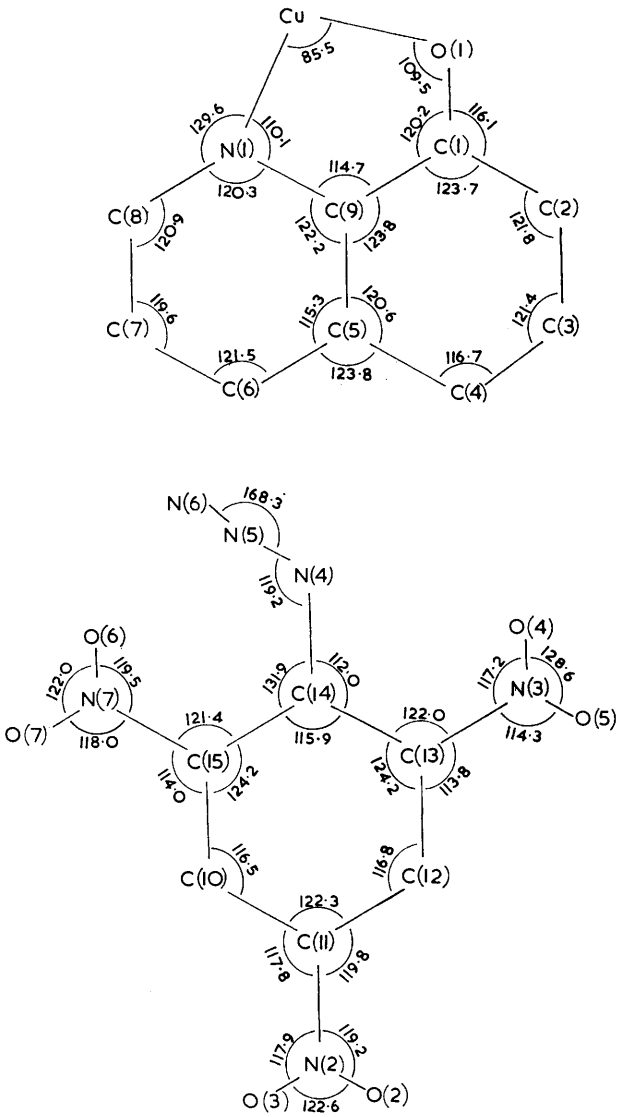


FIGURE 3. Inter-bond angles

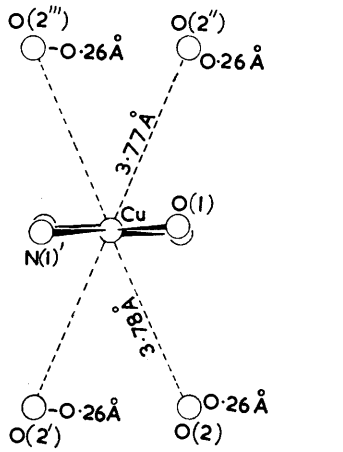


FIGURE 4. The environment of the copper atoms

the least-squares best plane of the benzene ring. The mean and maximum deviations of the ring-carbon atoms from this plane are 0·012 and 0·022 Å, respectively. The plane of the benzene ring and the plane of the quinoline system are only 2° out of parallel. The planes of the nitro-groups at C(11), C(13), and C(15) and the azido-group at C(14) make

[3] G. Polinck, *Acta Cryst.*, 1964, **17**, 687; F. Kanamaru, K. Ogawa, and I. Nitta, *Bull. Chem. Soc. Japan*, 1963, **36**, 422; J. A. Bevan, D. P. Graddon, and J. F. McConnell, *Nature*, 1963, **199**, 373.
[4] H. M. Powell and C. K. Prout, following Paper.

their respective angles of 7, 58, 14, and 20° with the benzene ring. The nitro-group at C(11) is out of plane in the opposite sense to the other three groups.

The benzene nucleus has internal angles greater than 120° at the carbon atoms attached to nitro-groups. In isolation, these differences are probably within the error of the determination but, when looked at together with other recent results [5-9] from work on nitrobenzene derivatives (Figure 6), they must be presumed to represent a real effect.

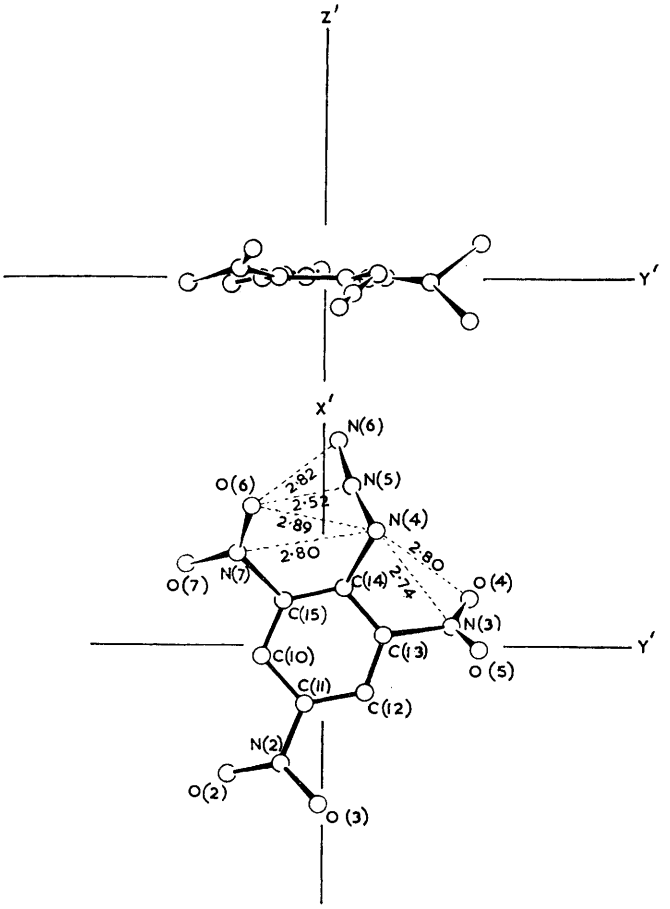


FIGURE 5. The picryl azide molecule projected parallel to, and perpendicular to, the least-squares best plane of the benzene nucleus

This effect appears rather general in such compounds, and is independent of the angle between the nitro-group and the plane of the ring. The nitro-groups show no anomalies but the azido-group is not linear. The angle at the central nitrogen atom N(5) is 168·3° with a standard deviation of 1·8° and, whereas the angle at N(4) is not sensibly different from the expected 120°, there is considerable distortion at C(14). The nitrogen atoms N(5) and N(6) must be very strongly repelled by the oxygen O(6), and the observed

[5] J. Trotter, *Acta Cryst.*, 1959, **12**, 884.
[6] J. Trotter, *Acta Cryst.*, 1961, **14**, 244.
[7] P. Copper, *Acta Cryst.*, 1964, **17**, 373.
[8] D. S. Brown, S. C. Wallwork, and A. Wilson, *Acta Cryst.*, 1964, **17**, 168.
[9] A. W. Hanson, *Acta Cryst.*, 1964, **17**, 559.

distortions suggest that there is some flexibility at N(5) and C(14), but that the configuration at N(4) is very rigid. Interest in the bending of the azide group has appeared recently in the field of reaction mechanisms. A synchronous mechanism [10] in which both N–C bonds are formed at the same time has been suggested for the addition of an organic azide to a C:C double bond. For this to happen, the rod-like azide group must bend at the central nitrogen atom. Calculations by Roberts [11] have suggested that the energy required for this bending would be expected to be quite small. The bending of the azide group in this molecule may be due to the overcrowding forced on it by the particular environment in this crystal. However, it is noteworthy that picryl azide reacts with a variety of

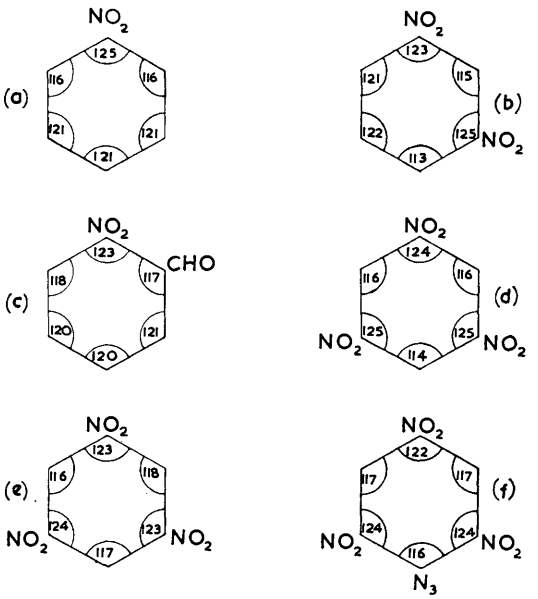


FIGURE 6. Inter-bond angles in nitrobenzene derivatives (a) nitrobenzene,[5] (b) *m*-dinitrobenzene,[6] (c) *o*-nitrobenzaldehyde,[7] (d) *sym.*-trinitrobenzene in the *sym.*-trinitrobenzene–anthracene complex,[8] (e) *sym.*-trinitrobenzene in the *sym.*-trinitrobenzene–indole complex,[9] and (f) picryl azide in the present picryl azide–bis-8-hydroxyquinolinato-copper(II) complex

olefins, norbornene, α-pinene, cyclopentene, cyclo-octene, and others, with exceptional ease.[12]

The molecule is clearly overcrowded in the region of the azide group, the very short non-bonded contacts (Figure 5) could be reduced if the nitro-groups at C(13) and C(15) and the azide group were all perpendicular to the plane of the benzene ring in a position similar to that observed in free picryl chloride [13] and iodide.[14] If this were so in this adduct, the present molecular packing could not occur, since the oxygen atoms O(6) and O(7) would make contacts of about 2·5—2·6 Å at the carbon atom C(2) of the metal oxinate. Also, the intermolecular contacts between the azide nitrogen atoms and the oxygen atoms O(4) and O(5) of a nitro-group of a neighbouring picryl azide molecule would be considerably shortened (Figure 2). It seems highly probable that this (Figure 5) is not the configuration of the free molecule, but is a result of a highly stable crystal structure.

In the " polarisation bonded " stacks, the relationship of the benzene system of the acceptor, picryl azide, and the quinoline system of the donor is that suggested by Mulliken for maximum π-overlap, and therefore for maximum stabilisation from charge-transfer effects. This is consistent with the observed charge-transfer band at 19,600 cm.$^{-1}$, which

[10] R. Huisgen, *Proc. Chem. Soc.*, 1961, 357; *Angew. Chem. Internat. Edn.*, 1963, **2**, 633.
[11] J. D. Roberts, *Chem. Ber.*, 1961, **94**, 273.
[12] A. S. Bailey, J. J. Merer, and J. D. White, unpublished results.
[13] G. A. Gol'der, G. S. Zhdanow, and M. M. Umansky, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 311.
[14] H. M. Powell and G. Hase, *J.*, 1941, 1398.

is polarised perpendicular to the molecular planes; [15] that is, the absorption of light at this frequency is a maximum when the electrical vector lies along the needle axis of the crystal. If the nitro-group at N(7) or the azide group were to move farther out of the plane, this nice system would be upset. It is perhaps noteworthy in this context that the energy of charge-transfer between donor and acceptor is not abnormally high for the 1 : 1 complexes bis-8-hydroxyquinolinatocopper(II) benzotrifuroxan [4] and bis-8-hydroxyquinolinatopalladium(II) chloroanil [16] in which the arrangement of the π-system in the donor and the acceptor must give rise to poor " overlap." The arrangement of donor and acceptor with respect to each other in the picryl azide complex is essentially the same as that observed in the 1,3,5-trinitrobenzene complexes of naphthalene,[17] indole, and skatole.[9]

The stability of the structure must be further enhanced by the neat interlocking of picryl azide molecules and copper complexes when the molecular stacks are brought together to give the complete crystal lattice.

Experimental

Preparation.—The crystals were prepared by the method described by Bailey, Williams, and Wright.[15]

X-Ray Photography.—The unit-cell dimensions were obtained from zero-layer Weissenberg photographs about the *a*- and *c*-axes calibrated by means of the diffraction pattern of a copper wire. *X*-Ray intensities were estimated visually from sets of multiple-film Weissenberg photographs about the *c*-axis. The values from individual layers were placed on a common scale by using the exposure time of the films to *X*-rays from a stabilised source and carefully standardised developing conditions. The intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction.

Calculations.—These were carried out on a Ferranti Mercury computer. Structure factors and cycles of least-squares refinement were calculated by Rollett's SFLS programme.[18] Atomic scattering factors for nitrogen carbon, and oxygen were as given by Berghuis *et al.*,[19] for hydrogen by McWeeny,[20] and for copper by Thomas and Umeda [21] with a correction for anomalous dispersion.[22] For Fourier syntheses Mills's general Fourier [18] programme was used, and for interatomic distances and angles Sparks's programme.[18]

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[15] A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J.*, 1965, 2579.
[16] B. Kamenar, C. K. Prout, and J. D. Wright, preceding Paper.
[17] S. C. Wallwork, *J.*, 1961, 494.
[18] O. S. Mills and J. S. Rollett in " Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon, London, 1961, p. 107.
[19] J. Berghius, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendal, *Acta Cryst.*, 1955, **8**, 478.
[20] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.
[21] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[22] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, 1955, **8**, 841.