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Crystal Structure of the Bis-(5,5′-diethylbarbiturato)bispyridine Complex of Copper(II)

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The crystal structure of the bis-(5,5′-diethylbarbiturato)bispyridine complex of copper(II) has been determined by Patterson and Fourier methods and refined by full-matrix least-squares computations to a final R of 0·036 for 1236 independent reflexions with measurable intensities. The monoclinic unit cell, space group $P2_1/c$, with $a=11{\cdot}235$, $b=9{\cdot}958$, $c=12{\cdot}624$ Å and $\beta=102{\cdot}6°$, contains two centrosymmetric molecules. The copper atom is bonded to the deprotonated nitrogen atoms of the barbital anions and the nitrogens of the pyridines, with bond lengths Cu–N of 1·983 (5) and 2·032 (5) Å respectively. There is evidence of off-the-z-axis coordination by oxygen atoms from the barbital moieties, which have a Cu–O distance of 2·722 (5) Å. The molecules are joined by relatively short (2·86 Å) N–H···O hydrogen bonds.

Introduction

We report the first determination of the crystal structure of a complex of copper(II) with a drug-active barbiturate as one of the ligands. Various complexes of transition metals with barbiturates have been prepared as they are important in the detection and identification of the drugs. They have the general formula M(II) $(barb)_2L_2$, where M is a transition metal, barb is the anion of a substituted barbituric acid and L is an organic base, usually pyridine.

Levi & Hubley (1956) have studied the reaction of copper with twelve different barbiturates in the presence of pyridine and, on the basis of infrared spectral data, have suggested that the barbiturate ligand is bound to the copper through an oxygen atom. More recently, the molecular structures of two complexes M(II) $(barb)_2(imidazole)_2$, (M = Co and Zn), have been elucidated by X-ray diffraction (Wang & Craven, 1971) and this study showed that, in both complexes, the donor atom in the barbiturate anion is a deprotonated nitrogen atom. The coordination environment of the metal atoms Co and Zn in these complexes is tetrahedral, each molecule possessing twofold crystallographic symmetry. The present X-ray analysis was undertaken in order to determine the molecular structure of the copper complex in which square-planar coordination was expected. It was also desirable to establish whether the barbiturate donor atom is N or O in the copper complex. Hydrogen bonding has been a prominent feature in the crystal structures of barbiturates, their salts (Berking & Craven, 1971; Craven, Vizzini & Rodrigues, 1969; Berking, 1972) and in the complexes M(II) $(barb)_2(imidazole)_2$ (Wang & Craven, 1971).

Experimental

Single crystals of the complex were obtained in the following manner: dilute aqueous solutions of $CuCl_2.2H_2O$, pyridine and sodium barbital were mixed in the molar ratio 1:2:2. The final pH of the mauve solution was 7·2. The crystals grew as small hexagonal plates. Microanalysis showed that they had the composition $CuC_{26}H_{32}N_6O_6$ corresponding to the formulation Cu(II) $(5,5'diethylbarbiturato)_2(pyridine)_2$. A single crystal of dimensions 0·25 × 0·225 × 0·35 mm was selected for the X-ray investigation. The lattice

Table 1. *Crystal data*

Molecular formula	$CuC_{26}H_{32}N_6O_6$
M.W.	587·5
Space group	$P2_1/c$ (Monoclinic, 2nd setting)
$a=11{\cdot}235$ (5) Å	$D_m=1{\cdot}410$ g cm^{-3}
$b=9{\cdot}958$ (4)	$D_c=1{\cdot}415$ g cm^{-3} for $Z=2$
$c=12{\cdot}624$ (5)	$\mu=8{\cdot}74$ cm^{-1}
$\beta=102{\cdot}6$ (2)°	$F(000)=614$
$V=1378{\cdot}54$ Å^3	

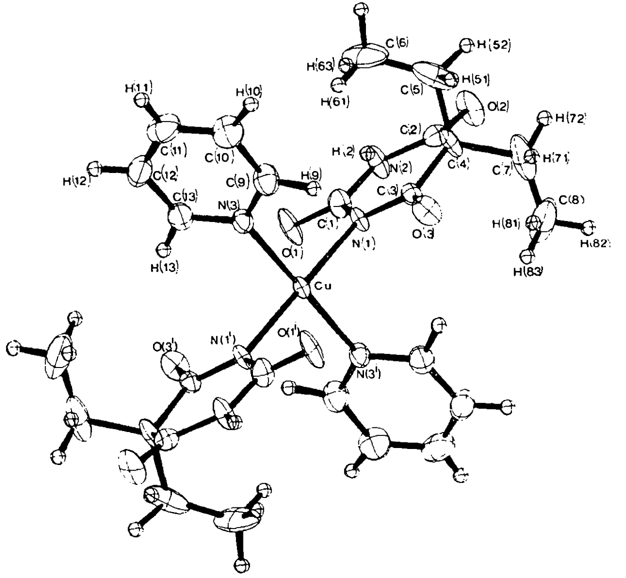

Fig. 1. The molecular structure of the complex. The superscripted atoms are centrosymmetrically related to the corresponding atoms without superscripts.

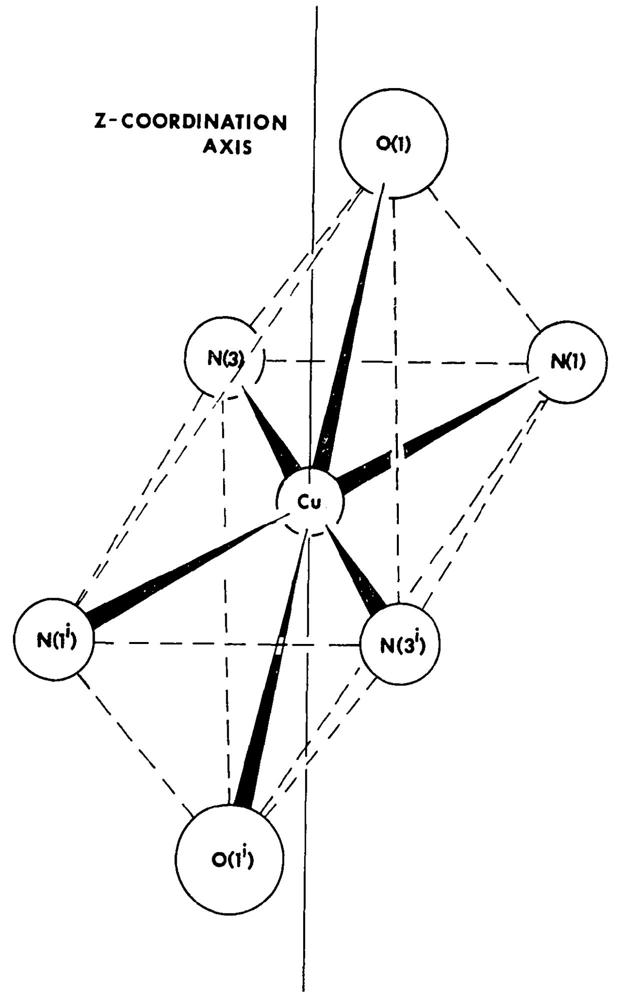

Fig. 2. The environment of the copper atom showing the 'off-the-z-axis' coordination involving O(1) and O(1ⁱ).

constants were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The crystal data are listed in Table 1. The crystal density was determined with a density-gradient column containing the components *m*-xylene ($\varrho = 0{\cdot}86$ g cm^{-3}) and carbon tetrachloride ($\varrho = 1{\cdot}60$ g cm^{-3}), which was precalibrated with aqueous caesium chloride solutions.

The intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the ω-scan mode (scan width = 0·9°, scan speed = 0·03° sec^{-1}).

With Zr-filtered Mo $K\alpha$ radiation, 1462 reflexions up to $2\theta = 40°$ were measured. Throughout the data collection, three reference reflexions were recorded after every 56 measured reflexions. The intensities of the standard reflexions remained constant to within ±2% throughout the run. Of the 1462 reflexions counted, 101 were systematically absent. Adopting the criterion of $I_{\text{rel}} > 2\sigma(I_{\text{rel}})$ for an observed reflexion, 116 reflexions were omitted as unobserved. A further nine reflexions were redundant due to space-group equivalence, leaving 1236 unique reflexions, all of which were employed in the structural determination. The data were corrected for Lorentz–polarization effects. For the crystal selected, μR varied between 0·10 and 0·15 and the maximum variation in the corresponding A^* values was between 1·18 and 1·28 for all θ values. This was deemed too small to warrant absorption corrections, which were therefore neglected.

Solution and refinement of the structure

With the copper atom at the unit-cell origin, the three-dimensional Patterson vector map resembles the elec-

Table 2. *Fractional atomic coordinates and thermal parameters and their e.s.d.'s for* Cu(II) *(5,5′-diethylbarbiturate)$_2$(pyridine)$_2$*

(*a*) Heavy atoms. Coordinates are ×10⁴. Thermal parameters are of the form

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{31}lh) \times 10^4\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Cu	0	0	0	22 (1)	47 (1)	18 (1)	−9 (1)	3 (1)	−2 (1)
C(1)	1304 (6)	1941 (7)	−770 (6)	40 (6)	75 (8)	31 (6)	−6 (6)	6 (5)	7 (6)
C(2)	3180 (6)	3176 (6)	−3 (5)	50 (7)	47 (8)	36 (5)	5 (6)	9 (5)	3 (5)
C(3)	2087 (5)	1705 (6)	1153 (5)	31 (6)	50 (8)	27 (6)	−2 (5)	7 (5)	−12 (5)
C(4)	3038 (6)	2791 (7)	1138 (5)	47 (6)	86 (9)	25 (5)	−32 (6)	−9 (4)	−1 (5)
C(5)	2640 (8)	4097 (8)	1641 (6)	149 (11)	85 (10)	45 (6)	−59 (9)	28 (7)	−25 (6)
C(6)	1416 (8)	4656 (8)	1126 (7)	132 (10)	68 (10)	117 (9)	5 (8)	71 (8)	−39 (8)
C(7)	4278 (7)	2313 (10)	1796 (6)	63 (7)	181 (14)	50 (6)	−49 (9)	−22 (6)	43 (8)
C(8)	4743 (7)	1066 (10)	1362 (8)	51 (8)	146 (13)	150 (10)	18 (8)	6 (7)	78 (10)
C(9)	−1009 (6)	2023 (7)	1264 (6)	49 (7)	96 (10)	41 (6)	0 (6)	10 (5)	−6 (6)
C(10)	−1813 (7)	2989 (8)	1503 (6)	63 (8)	111 (10)	54 (6)	8 (7)	24 (6)	−20 (7)
C(11)	−2854 (7)	3253 (7)	748 (7)	63 (8)	74 (9)	98 (8)	11 (7)	41 (7)	0 (7)
C(12)	−3070 (6)	2569 (8)	−226 (7)	44 (7)	78 (9)	77 (7)	8 (7)	6 (5)	16 (7)
C(13)	−2230 (6)	1644 (7)	−427 (5)	46 (7)	70 (9)	47 (6)	−2 (7)	7 (5)	−6 (6)
N(1)	1294 (4)	1390 (5)	226 (4)	25 (5)	57 (6)	20 (4)	−16 (4)	2 (4)	−7 (4)
N(2)	2234 (5)	2819 (5)	−844 (4)	43 (5)	94 (7)	15 (4)	−31 (5)	−1 (4)	10 (4)
N(3)	−1217 (4)	1366 (5)	323 (4)	32 (5)	61 (6)	33 (4)	1 (5)	6 (4)	−13 (5)
O(1)	530 (4)	1638 (5)	−1562 (4)	56 (4)	136 (7)	19 (3)	−41 (5)	−15 (3)	−5 (4)
O(2)	4040 (4)	3789 (5)	−171 (4)	47 (5)	104 (6)	58 (4)	−46 (5)	13 (3)	28 (4)
O(3)	2031 (4)	1162 (4)	2009 (3)	67 (5)	78 (5)	14 (3)	−16 (4)	11 (3)	5 (4)

Table 2 (*cont.*)

(*b*) Fractional atomic coordinates (× 10^3) and their e.s.d.s' for the hydrogen atoms.

	x	*y*	*z*
H(2)	231 (5)	316 (7)	−154 (5)
H(51)	269 (7)	385 (8)	236 (6)
H(52)	336 (7)	472 (7)	170 (6)
H(71)	414 (6)	216 (8)	257 (6)
H(72)	480 (6)	312 (8)	184 (6)
H(61)	73 (7)	401 (8)	125 (7)
H(62)	124 (7)	556 (7)	159 (7)
H(63)	132 (7)	464 (7)	29 (7)
H(81)	478 (8)	116 (8)	71 (7)
H(82)	549 (7)	79 (8)	184 (7)
H(83)	424 (7)	25 (8)	155 (7)
H(9)	−26 (6)	170 (7)	184 (5)
H(10)	−156 (6)	341 (7)	223 (6)
H(11)	−334 (6)	382 (7)	94 (6)
H(12)	−381 (6)	275 (7)	−77 (6)
H(13)	−237 (6)	108 (7)	−114 (5)

tron density map. However, since the Patterson map had *P*2/*m* symmetry, care was exercised in selecting unique peaks from their corresponding mirror images. Nine atomic positions were found by analysis of the Patterson function and all the remaining non-hydrogen atoms were located on inspection of a subsequent Fourier synthesis. Scattering factors for the copper, carbon, nitrogen, oxygen and hydrogen atoms were those obtained from the HFS model (Hanson, Herman, Lea & Skillman, 1964). The copper was treated as Cu^0 and the anomalous dispersion correction ($\Delta f' = 0{\cdot}3$ for Mo $K\alpha$ radiation) was applied to the scattering curve. The positional and anisotropic temperature factors of all the non-hydrogen atoms were refined by the method of least squares (*ORFLS*: Busing, Martin & Levy, 1963), each of the 1236 reflexions being assigned unit weight. In the last cycle of non-hydrogen atom refine-

Table 3. *Observed and calculated structure factors*

The values listed are $10F_o$ and $10F_c$.

h	l	F_o	F_c
k = -10			
-3	4	138	-148
-3	3	277	270
-3	2	63	-69
-3	1	314	325
-3	0	171	185
-2	0	85	80
-2	1	248	258
-2	2	132	148
-2	3	79	84
-2	4	379	383
-2	6	246	246
-1	6	81	-85
-1	5	210	212
-1	3	116	116
-1	2	147	149
-1	1	186	194
-1	0	179	-186
0	0	472	490
0	2	407	409
0	4	244	243
0	6	268	269
k = -9			
-5	0	85	-83
-5	1	162	172
-5	2	103	-110
-5	3	56	43
-4	6	194	187
-4	5	104	106
-4	4	95	71
-4	3	79	-83
-4	2	153	149
-4	1	38	-34
-4	0	251	265
-3	0	36	51
-3	1	122	132
-3	2	120	123
-3	3	220	229
-3	4	201	205
-3	5	310	309
-3	6	125	130
-3	7	309	303
-2	8	149	144
-2	7	85	-82
-2	6	272	271
-2	5	103	-106
-2	4	324	316
-2	3	75	-75
-2	2	301	293
-2	1	85	92
-2	0	123	120
-1	1	356	370
-1	2	44	-34
-1	3	319	324
-1	4	68	-59
-1	5	304	309
-1	7	230	220
-1	8	146	142
0	8	393	382
0	6	98	92
0	4	364	375
0	2	392	413
0	0	486	498
k = -8			
-6	0	207	215
-6	1	104	-108
-6	2	159	148
-6	4	221	217
-5	5	181	171
-5	4	116	111
-5	3	140	133
-5	2	87	74
-5	1	371	383
-5	0	51	37
-4	0	123	123
-4	1	126	138
-4	2	285	295
-4	3	37	-23
-4	4	180	181
-4	5	86	109
-4	6	168	166
-4	7	50	-41
-4	8	119	129
-3	8	39	23
-3	7	177	174
-3	6	49	-50
-3	5	209	205
-3	3	64	57
-3	1	109	121
-2	0	504	522
-2	2	298	303
-2	4	277	270
-2	5	129	128
-2	6	464	462
-2	7	191	200
-2	8	424	406
-2	9	352	351
-1	9	321	308
-1	8	158	160
-1	7	357	355
-1	6	42	-52
-1	5	412	405
-1	4	42	-32
-1	3	505	508
-1	2	181	-171
-1	1	283	283
0	0	212	220
0	2	453	460
0	4	417	424
0	6	45	-20
0	8	146	149
k = -7			
-7	0	97	-98
-7	1	121	127
-7	2	47	-66
-7	3	261	252
-7	4	42	-74
-6	5	134	128
-6	4	254	260
-6	3	132	-130
-6	2	258	244
-6	1	66	69
-6	0	215	214
-5	0	179	178
-5	1	206	205
-5	2	69	75
-5	3	213	202
-5	4	56	-57
-5	5	346	353
-5	6	60	-63
-5	7	106	118
-5	8	230	-211
-4	9	206	-219
-4	8	157	167
-4	7	156	-170
-4	6	179	186
-4	4	194	191
-4	2	120	118
-4	1	33	-22
-4	0	384	385
-3	1	337	344
-3	3	175	166
-3	4	112	134
-3	5	379	384
-3	6	55	55
-3	7	370	374
-3	8	268	272
-3	9	292	286
-2	10	187	176
-2	9	342	334
-2	8	444	422
-2	7	165	163
-2	6	295	274
-2	5	33	45
-2	4	35	50
-2	3	132	144
-2	2	220	226
-2	1	398	-406
-2	0	297	305
-1	0	97	-92
-1	1	337	338
-1	2	245	248
-1	3	563	573
-1	4	247	251
-1	5	279	275
-1	6	57	55
-1	7	270	262
-1	9	271	167
-1	10	111	-97
0	10	378	385
0	8	213	217
0	6	455	440
0	4	815	807
0	2	823	822
0	0	489	485
k = -6			
-7	6	66	66
-7	5	306	313
-7	4	142	155
-7	3	147	139
-7	2	106	117
-7	1	227	220
-7	0	79	80
-6	0	290	286
-6	1	161	-172
-6	2	349	364
-6	3	89	-87
-6	4	475	465
-6	5	199	196
-6	6	301	282
-6	7	158	-174
-5	9	198	198
-5	8	133	-132
-5	7	178	-169
-5	6	166	-158
-5	5	249	146
-5	4	98	-118
-5	3	611	602
-5	2	170	-171
-5	1	117	112
-5	0	110	123
-4	0	439	436
-4	1	119	112
-4	2	330	337
-4	3	73	-67
-4	4	324	322
-4	5	77	-65
-4	6	298	287
-4	7	279	294
-4	8	472	472
-4	9	161	155
-3	10	50	46
-3	9	283	262
-3	8	129	142
-3	7	489	478
-3	5	249	244
-3	4	75	-86
-3	3	115	129
-3	2	149	152
-3	1	280	284
-2	0	416	426
-2	1	96	109
-2	2	317	320
-2	3	334	336
-2	4	83	85
-2	5	143	-142
-2	6	236	241
-2	7	52	-45
-2	8	306	302
-2	9	124	-117
-2	10	237	233
-1	11	397	392
-1	9	223	219
-1	8	74	75
-1	7	306	312
-1	6	40	42
-1	5	526	527
-1	4	112	108
-1	3	573	549
-1	2	170	167
-1	1	589	586
-1	0	180	-181
0	0	224	231
0	2	251	252
0	4	557	546
0	6	568	550
0	8	162	158
0	10	310	312
k = -5			
-8	4	202	196
-8	3	99	95
-8	2	160	160
-8	1	62	-62
-8	0	243	244
-7	0	159	163
-7	1	178	167
-7	2	117	110
-7	3	74	76
-7	4	61	49
-7	5	85	103
-7	6	180	-178
-7	7	140	135
-6	8	222	212
-6	7	155	-162
-6	6	239	234
-6	5	73	63
-6	4	308	288
-6	3	171	162
-6	2	182	178
-6	0	241	256
-5	1	565	555
-5	2	93	-98
-5	3	758	745
-5	4	39	47
-5	5	476	458
-5	6	305	316
-5	7	412	404
-5	8	347	345
-5	9	238	229
-4	10	71	71
-4	9	142	131
-4	8	287	280
-4	7	327	319
-4	6	354	338
-4	5	77	68
-4	4	138	127
-4	3	265	-254
-4	2	204	208
-4	1	105	-107
-4	0	241	252
-3	0	33	36
-3	1	550	549
-3	2	50	55
-3	3	340	338
-3	4	98	-91
-3	5	87	97
-3	6	157	-145
-3	7	467	455
-3	8	275	-271
-3	9	303	294
-3	11	165	173
-2	10	297	309
-2	9	298	-282
-2	8	435	449
-2	7	179	-179
-2	6	387	395
-2	5	31	28
-2	4	573	560
-2	3	155	149
-2	2	666	638
-2	1	283	249
-2	0	533	531
-1	0	319	-304
-1	1	367	361
-1	2	79	83
-1	3	368	369
-1	4	194	-179
-1	5	503	495
-1	6	164	-169
-1	7	57	58
-1	8	61	-51
-1	9	269	265
-1	11	362	350
0	10	312	319
0	8	163	158
0	6	690	480
0	4	381	379
0	2	54	63
0	0	279	283
k = -4			
-8	0	122	127
-8	1	76	-66
-8	2	137	128
-8	3	84	96
-8	4	225	229
-8	5	147	-148
-7	7	50	56
-7	6	191	-198
-7	5	47	46
-7	4	84	-85
-7	3	190	193
-7	2	80	-89
-7	1	338	324
-7	0	163	-165
-6	0	214	214
-6	1	123	119
-6	2	101	95
-6	3	246	256
-6	4	175	174
-6	5	201	214
-6	6	289	284
-6	7	302	304
-6	8	171	171
-6	9	85	77
-5	9	83	68
-5	8	195	209
-5	7	194	461
-5	6	291	295
-5	5	388	572
-5	4	105	94
-5	3	192	206
-5	2	46	-46
-5	1	108	127
-5	0	88	79
-4	0	426	427
-4	2	1078	1079
-4	3	116	119
-4	4	726	709
-4	5	78	51
-4	6	440	435
-4	7	151	-152
-4	8	316	325
-4	9	57	-42
-4	10	285	289
-3	11	359	360
-3	9	430	441
-3	8	102	85
-3	7	328	344
-3	4	221	-227
-3	3	777	764
-3	2	165	153
-3	1	1268	1274
-3	0	109	102
-2	0	355	363
-2	1	37	32
-2	2	295	299
-2	3	502	-492
-2	4	325	327
-2	5	166	-171
-2	6	524	527
-2	7	363	-354
-2	8	385	373
-2	9	147	-139
-2	10	172	163
-2	11	60	-65
-1	11	184	184
-1	9	366	364
-1	8	347	-321
-1	7	243	241
-1	6	280	-271
-1	5	514	528
-1	4	42	-40
-1	3	233	239
-1	2	71	67
-1	1	44	51
-1	0	160	350
0	0	311	315
0	2	510	-476
0	4	369	350
0	6	188	197
0	8	156	160
0	10	284	286
k = -3			
-9	0	98	-100
-9	1	241	249
-9	2	69	-80
-9	3	359	369
-8	5	169	-166
-8	4	57	74
-8	2	258	257
-8	1	98	107
-8	0	202	199
-7	0	74	-68
-7	1	138	141
-7	2	55	62
-7	3	288	274
-7	4	141	150
-7	5	224	222
-7	6	310	315
-7	7	158	157
-7	8	173	175
-6	9	50	49
-6	8	175	163
-6	7	266	261
-6	6	360	358
-6	5	61	-70
-6	4	265	252
-6	3	87	-78
-6	2	65	64
-6	0	191	198
-5	0	180	178
-5	1	200	219
-5	2	283	267
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-1	2	81	79
-1	3	312	316
-1	4	160	-158
0	4	278	285
0	2	469	474
k = 10			
-3	0	184	-185
-2	0	86	80
-1	1	193	189
-1	0	188	186
0	2	328	328

ment, the average e.s.d. in the positional and anisotropic temperature factors was about fifty times the average parameter shift. All the hydrogen atoms were located from subsequent difference syntheses and were assigned the temperature factors of the atoms to which they were bonded. After the last refinement cycle, in which the hydrogen atomic positions were varied, the average e.s.d. in these parameters was about ten times the average parameter shift. The last cycle of refinement yielded an *R* of 0·036. The final atomic positional and thermal parameters are listed in Table 2(*a*) and (*b*).

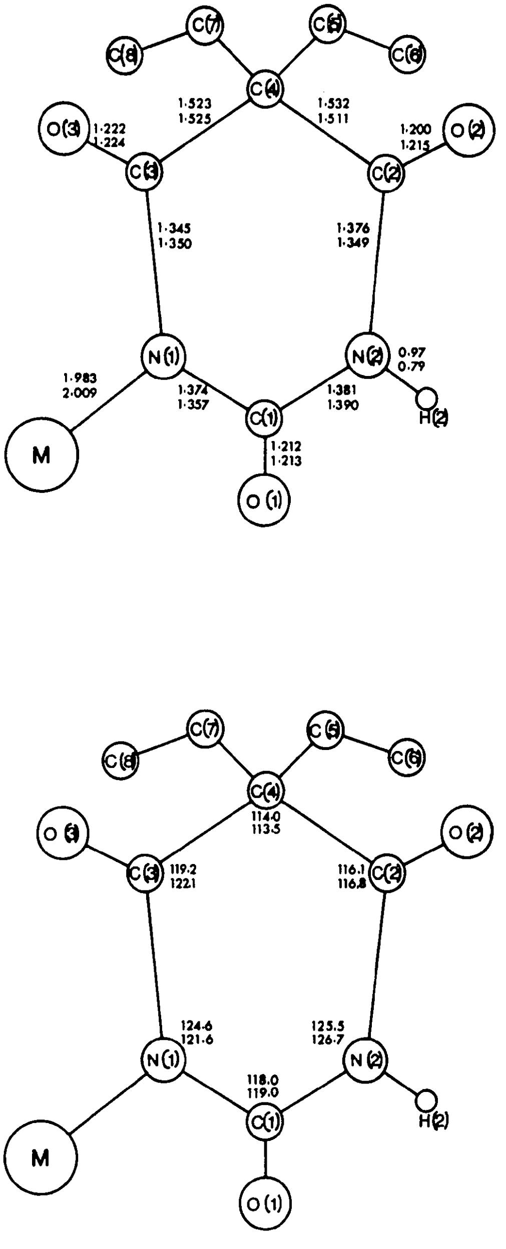

Fig. 3. Relevant bond lengths (Å) and bond angles (°) for the barbital moiety in Cu(II)(barb)$_2$ (pyridine)$_2$ (upper number) and in Zn(II)(barb)$_2$(imidazole)$_2$ (lower number).

As a final check of the correctness of the structure, a difference synthesis with the structure factors calculated in the last cycle of the refinement was computed. This map was practically featureless. The observed and calculated structure factors are listed in Table 3.

Description of the structure and discussion

Intramolecular bond distances and angles with their e.s.d.'s from the least-squares refinement are listed in Tables 4 and 5 respectively. These parameters were calculated with the *X-RAY* (1972) program system. Table 6 lists computed least-squares planes with their equations and the distances of various atoms from these planes. The molecular structure is shown in Fig. 1 (*ORTEP*: Johnson, 1965).

Table 4. *Intramolecular bond lengths and their e.s.d.'s* (Å)

Cu—N(1)	1·983 (5)	C(11)–C(12)	1·38 (1)
Cu—N(3)	2·032 (5)	C(12)–C(13)	1·38 (1)
C(1)—N(1)	1·374 (9)	N(2)—H(2)	0·97 (6)
C(3)—N(1)	1·345 (8)	C(9)—H(9)	1·04 (6)
C(1)—N(2)	1·381 (9)	C(10)–H(10)	1·00 (7)
C(2)—N(2)	1·376 (8)	C(11)–H(11)	0·86 (7)
C(9)—N(3)	1·332 (9)	C(12)–H(12)	0·97 (6)
C(13)–N(3)	1·342 (8)	C(13)–H(13)	1·04 (7)
C(1)—O(1)	1·212 (8)	C(5)—H(51)	0·93 (7)
C(2)—O(2)	1·200 (9)	C(5)—H(52)	1·01 (8)
C(3)—O(3)	1·222 (8)	C(7)—H(71)	1·03 (8)
C(2)—C(4)	1·532 (9)	C(7)—H(72)	0·98 (8)
C(3)—C(4)	1·523 (9)	C(6)—H(61)	1·04 (8)
C(4)—C(5)	1·56 (1)	C(6)—H(62)	1·11 (8)
C(5)—C(6)	1·49 (1)	C(6)—H(63)	1·04 (8)
C(4)—C(7)	1·53 (1)	C(8)—H(81)	0·84 (9)
C(7)—C(8)	1·50 (1)	C(8)—H(82)	0·96 (7)
C(9)—C(10)	1·40 (1)	C(8)—H(83)	1·04 (8)
C(10)–C(11)	1·36 (1)		

Table 5. *Intramolecular bond angles* (°)

N(1)–Cu—N(1$^{\mathrm{I}}$)	180·0	N(1)—C(3)—O(3)	121·0 (6)
N(3)–Cu—N(3$^{\mathrm{I}}$)	180·0	C(4)—C(3)—O(3)	119·8 (5)
N(3)–Cu—N(1)	90·5 (2)	N(1)—C(3)—C(4)	119·2 (6)
N(1)–Cu—N(3$^{\mathrm{I}}$)	89·5 (2)	C(2)—C(4)—C(3)	114·0 (5)
Cu—N(1)–C(3)	127·9 (4)	C(5)—C(4)—C(7)	110·3 (6)
Cu—N(1)–C(1)	107·4 (4)	C(4)—C(5)—C(6)	116·9 (6)
C(1)–N(1)–C(3)	124·6 (5)	C(4)—C(7)—C(8)	114·0 (6)
C(1)–N(2)–C(2)	125·5 (6)	Cu—N(3)—C(9)	120·8 (4)
C(1)–N(2)–H(2)	120 (3)	Cu—N(3)—C(13)	120·1 (4)
C(2)–N(2)–H(2)	114 (3)	C(9)—N(3)—C(13)	119·1 (6)
N(1)–C(1)–O(1)	120·6 (6)	N(3)—C(9)—C(10)	122·3 (6)
N(2)–C(1)–O(1)	121·3 (6)	N(3)—C(13)–C(12)	121·1 (6)
N(1)–C(1)–N(2)	118·1 (5)	C(9)—C(10)–C(11)	118·6 (7)
N(2)–C(2)–O(2)	120·8 (6)	C(10)–C(11)–C(12)	119·0 (7)
C(4)–C(2)–O(2)	123·1 (5)	C(11)–C(12)–C(13)	119·9 (6)
N(2)–C(2)–C(4)	116·1 (6)		

Environment of the copper atom

The four nitrogen donor atoms are arranged in a square-planar configuration about the copper atom, the bond angles N(1)–Cu–N(3) and N(1)–Cu–N(3$^{\mathrm{I}}$) being 90·5 (2) and 89·5 (2)° respectively. The Cu–N(3) distance is 2·032 (5) Å, only very slightly longer than

Table 6. *Least-squares planes*

The equations of the planes are expressed in orthogonalized space as $PI+QJ+RK=S$.

Plane I: through atoms Cu, N(1), N(3), N(1ⁱ), N(3ⁱ)

Equation: $0\cdot04272I-0\cdot23816J+0\cdot97028K=0\cdot00$

Plane II: through the six pyrimidine ring atoms, C(3), N(1), C(1), N(2), C(2) and C(4).

Equation: $-0\cdot63299I+0\cdot76268J+0\cdot13278K=0\cdot24309$

Atoms included in calculation	Dist. from plane (Å)	Atoms not included in calculation	Dist. from plane (Å)
C(3)	−0·043	O(3)	−0·127
N(1)	−0·031		
C(1)	0·044	O(1)	0·097
N(2)	0·024		
C(2)	−0·094	O(2)	−0·296
C(4)	0·100		

Angle of intersection of planes I and II: 85·42°.

Plane III: through the six pyridine ring atoms, C(9), C(10), C(11), C(12), C(13), N(3)

Equation: $0\cdot58073I+0\cdot71496J-0\cdot38934K=-0\cdot02245$

Atoms included in calculation	Dist. from plane (Å)	Atoms not included in calculation	Dist. from plane (Å)
C(9)	−0·003	H(9)	−0·114
C(10)	0·007	H(10)	0·002
C(11)	−0·002	H(11)	−0·037
C(12)	−0·007	H(12)	−0·015
C(13)	0·011	H(13)	−0·031
N(3)	−0·006	Cu	0·022

Angle of intersection of planes I and III: 58·45°
Angle of intersection of planes II and III: 82·76°.

Plane IV: through the trioxopyrimidine ring atoms C(3), N(1)' C(1), N(2), C(2), C(4), O(1), O(2), O(3).

Equation: $-0\cdot59364I+0\cdot78876J+0\cdot15955K=0\cdot36558$

Atoms included in calculation	Dist. from plane (Å)
C(3)	−0·004
N(1)	−0·056
C(1)	0·012
N(2)	0·055
C(2)	0·007
C(4)	0·210
O(1)	0·006
O(2)	−0·146
O(3)	−0·085

Angle of intersection of planes II and IV: 3·11°
Angle of intersection of planes I and IV: 86·70°.

Plane V: through atoms C(5), C(6), C(7), C(8) of the diethyl group and atom C(4)

Equation: $-0\cdot58613I-0\cdot54894J+0\cdot59592K=-2\cdot48933$

Atoms included in calculation	Dist. from plane (Å)
C(4)	−0·018
C(5)	−0·020
C(6)	0·020
C(7)	0·016
C(8)	0·003

Angle of intersection of planes II and V: 88·2°.

the corresponding distance, Cu–N, of 1·989 (6) Å in the complex *trans*-bis[(chloroacetato)-(α-picoline)] copper(II) (Davey & Stephens, 1971). Of interest is the Cu–N(1) distance of 1·983 (5) Å. As no similar compounds containing copper bound to a barbiturate through the nitrogen atom are known, this distance may be compared with the analogous Co–N and Zn–N distances [2·020 (3) and 2·009 (2) Å respectively] found in the complexes M(II) (barb)$_2$(imidazole)$_2$. The plane through atoms Cu, N(1), N(3), N(1ⁱ) and N(3ⁱ) has been labelled plane I. Two further exocyclic barbiturate oxygen atoms O(1) and O(1ⁱ) are 2·723 (5) Å from the copper atom above and below plane I. They therefore appear to be involved in off-the-*z*-axis coordination (Fig. 2), which is also found in the complexes diacetatodiammine copper(II) (Siminov, Ablov & Malinovskii, 1963) (Cu···O 2·77 Å) and *trans*-bis[(chloroacetato)-(α-picoline)]copper(II) (Cu···O 2·707 Å) (Davey & Stephens, 1971). Atoms O(3) and O(3ⁱ), exocyclic barbiturate oxygen atoms, lie at a distance of 3·234 (7) Å from the copper atom, just less than 3·4 Å, the sum of the van der Waals radii of copper and oxygen. This further interaction, if present at all, is probably much weaker than the Cu···O(1) interaction. All distances and angles involving the copper coordination sphere are listed in Table 7. Considering the normal to the Cu, N(1), N(3) plane as the 'tetragonal' axis, *z*, for the complex (Fig. 2), then the angle between the 'out of plane' Cu–O(1) direction and the *z* axis is 35·7°. The analogous angle found in the complex *trans*-bis-

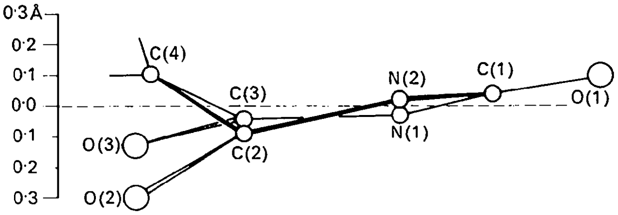

Fig. 4. The conformation of the trioxopyrimidine ring. The dotted line is a trace of the best least-squares plane through the six ring atoms only (plane II). The vertical scale is approximately three times the horizontal scale.

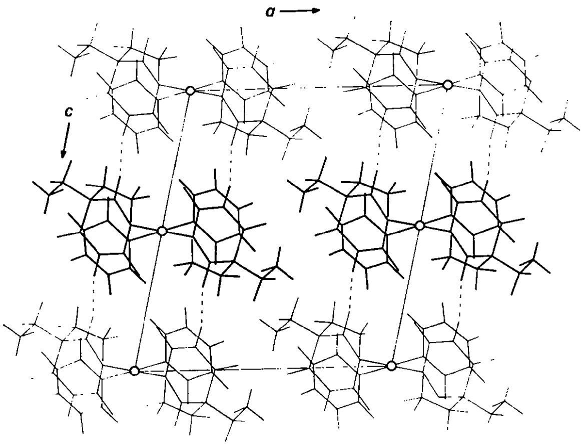

Fig. 5. The [010] projection of the structure. Intermolecular hydrogen bonding is represented by dotted lines.

[(chloroacetato)-(α-picoline)]copper(II) has a value of 36·1°.

Table 7. *Interatomic distances* (Å) *and bond angles* (°) *and their e.s.d.'s. in the copper coordination sphere*

Cu—N(1)	1·983 (5)	N(3)–Cu–O(1)	90·4 (2)
Cu—N(3)	2·032 (5)		
Cu—O(1)	2·723 (5)	N(1)–Cu–O(1)	54·3 (2)
N(3)–O(1)	3·409 (7)		
N(1)–O(1)	2·247 (7)	$N(3^i)$–Cu–O(1)	89·6 (2)
$N(3^i)$–O(1)	3·386 (7)		
$N(1^i)$–O(1)	4·200 (7)		
N(1)–N(3)	2·850 (7)		
N(1)–$N(3^i)$	2·827 (7)		

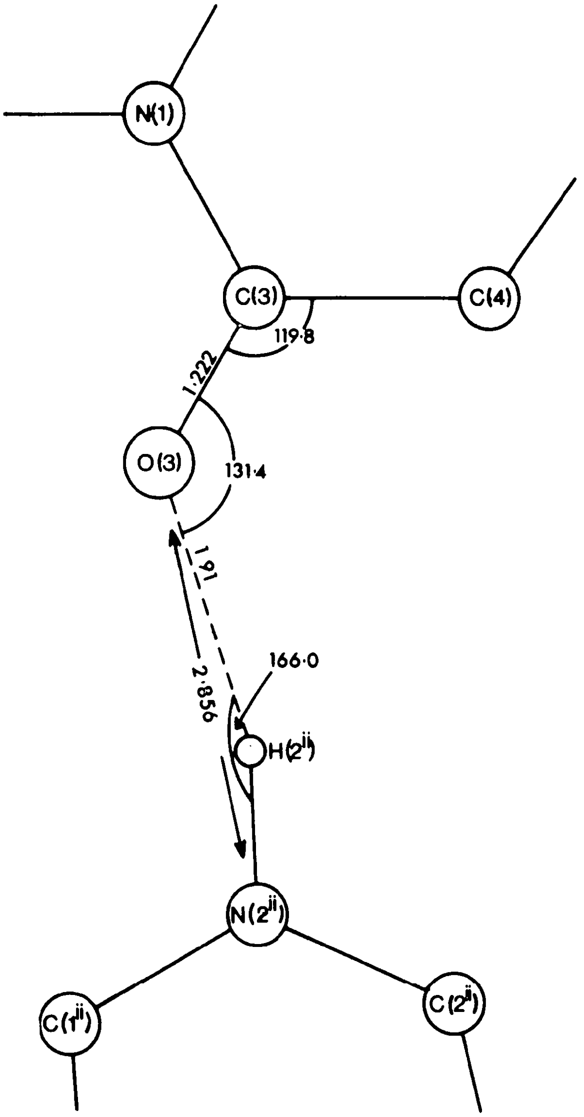

Fig. 6. Schematic drawing of the geometry of the intermolecular hydrogen bond. The bond drawn is that between a molecule at x,y,z (upper ring) and a molecule at $x,\frac{1}{2}-y,\frac{1}{2}+z$ (lower ring, superscripts ii).

In the pyridine moiety, the C–C and C–N bond lengths are within the expected ranges. The average C–H distance is 0·98 Å. The greatest deviation from the least-squares plane through the six pyridine ring atoms is that of atom C(13), 0·011 Å; (see Table 6). This plane has been labelled plane III. Planes I and III intersect at an angle of 58·45°.

The barbital ligand structure

In Fig. 3, a comparison is drawn between the bond lengths and bond angles in the system M-barb in the two complexes $Cu(barb)_2(pyridine)_2$ investigated here, and $Zn(barb)_2(imidazole)_2$. Generally there is good agreement among these parameters. Of interest is the bond angle C(1)–N(1)–C(3). On comparison of the parent barbituric acid with the barbital ion in the sodium salt, it was found (Berking & Craven, 1971) that as a result of deprotonation, the internal ring angle at N(1) closes from 126·4° in barbital to 119·2° in its ion. In the complex reported here, the angle C(1)–N(1)–C(3) is 124·6° which is close to the corresponding angle in the protonated barbital molecule (126·4°); thus, on chelation of the barbital ion through atom N(1), the angles around N(1) and its neighbouring ring carbon atoms in Cu(II) $(barb)_2(pyridine)_2$ revert from the values in the barbital ion to values close to those found in the barbital molecule, as expected.

The conformation of the trioxopyrimidine ring is shown in Fig. 4. The dotted line is a trace of the best least-squares plane through the six ring atoms (plane II). The exocyclic oxygen atoms have been included in the figure; the puckered conformation of the ring is evident.

Atoms C(5), C(6), C(7), C(8) together with atom C(4) form a hydrocarbon chain which is almost perpendicular (88·2°) to the pyrimidine ring plane. The hydrogen atoms of the diethyl group are in the staggered configuration.

Planes I and IV intersect at 86·7° *i.e.*, the plane Cu, N(1), N(3) and the trioxopyrimidine ring plane are almost perpendicular. Two relatively close intramolecular approaches may be mentioned. These are O(3)···H(9), 2·59 (6) Å, and O(3)···$H(13^i)$, 2·56 (7) Å, involving an exocyclic oxygen atom of the barbiturate ring and H atoms of the pyridine ring. These distances are close to the well-established O···H van der Waals sum of 2·6 Å.

From the analysis of the complex Zn(II) $(barb)_2$-$(imidazole)_2$, it was concluded that the configuration of the barbiturate and imidazole ligands is stabilized by C–H···O interactions involving carbon atoms of imidazole and carbonyl oxygen atoms of barbital at a C···O distance of 3·02 Å. The H···O distance is 2·37 (3) Å. In imidazole, the methine group involved is flanked by ring nitrogen atoms which may enhance the acidity of the hydrogen atom and favour a C–H···O interaction. In the present study, it was found that the distances C(9)···O(3) and $C(13^i)$···O(3) are both large, so that attractive C–H···O interactions in the complex Cu(II) $(barb)_2(pyridine)_2$ do not appear to be present. This is another factor (in addition to coordination type) which contributes to the small differences in the barbital ligands in the copper and zinc complexes (Fig. 3).

Intermolecular structure

The structure is dominated by intermolecular hydrogen bonding of the type N–H···O=C. There is only one crystallographically distinct hydrogen bond, N(2)–H(2)···O(3^{ii}) and this links adjacent barbital moieties in a zigzag pattern parallel to **c**. This is shown in Fig. 5, the [010] projection of the structure. There are thus four hydrogen bonds emanating from each molecule; two of these bonds link any two adjacent molecules.

The geometry of the interaction is shown in Fig. 6. The distances N(2)···O(3), N(2)···H(2), H(2)···O(3) are in good agreement with the corresponding distances in hydrogen-bonded systems in compounds containing donor ring-NH groups and acceptor carbonyl oxygen atoms (Donohue, 1968). The [001] projection, which shows no intramolecular overlap, is illustrated in Fig. 7.

All computations were performed on a Univac 1106 computer system.

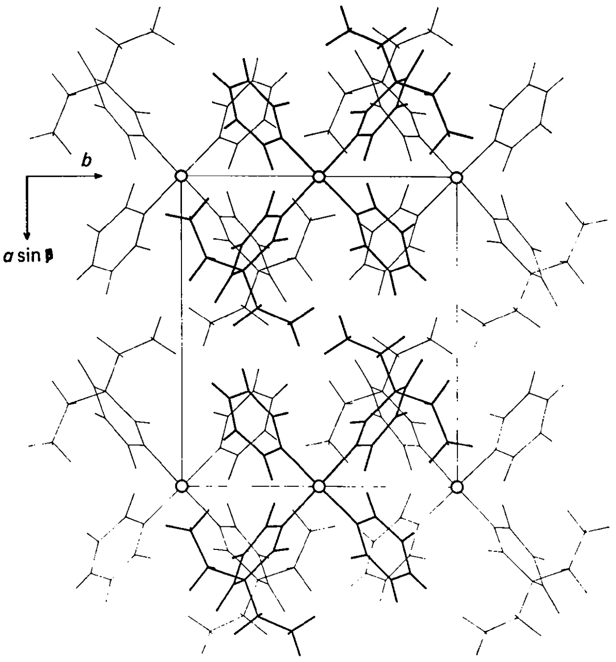

Fig. 7. The [001] projection of the structure.

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