

The Crystal and Molecular Structure of Dimeric Dibromobis(pyridine *N*-oxide) copper(II), [(pyridine *N*-oxide)₂ CuBr₂]₂

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The crystal and molecular structure of dimeric dibromobis(pyridine *N*-oxide) copper(II), [(C₅H₅NO)₂CuBr₂]₂, was determined by single-crystal X-ray diffraction techniques. This compound crystallizes in the triclinic system with $a = 10.510$ (2), $b = 10.883$ (1), $c = 11.818$ (5) Å, $\alpha = 78.57$ (3), $\beta = 89.88$ (3), $\gamma = 81.17$ (1)°, space group $P\bar{1}$, $\rho_o = 2.08$, $\rho_c = 2.10$ g.cm⁻³ and $Z = 2$. The structure was solved by Patterson and electron-density Fourier techniques and refined by block-diagonal least-squares analysis to a final R value of 0.046 based on 4415 observed reflections. The structure consists of two centrosymmetric dimeric molecules crystallographically non-equivalent. The centers of symmetry of the two molecules are located at the origin and at the center of the unit cell. In both dimers each copper atom is coordinated by two bromine atoms, and by three oxygen atoms of which two are bridging. The bromine atoms are located above and below the plane defined by the copper atoms and the bridging oxygen atoms. The two dimeric molecules show significant differences in some bond distances and angles and in the relative orientation of the pyridine *N*-oxide molecules. The geometry of this complex differs markedly from that of its chloride analog, as well as from that of other members of the aromatic *N*-oxide copper(II) halide series. The magnetic properties of the bromide complex are discussed in relation to those of related compounds.

Introduction

Aromatic *N*-oxides form complexes with more than 40 elements (Orchin & Schmidt, 1968), including all members of the first transition series. The stereochemistry of these systems is interesting as the oxygen atom may act as a monodentate ligand, as a bridging ligand, or as both in the same structure. Consequently, monomeric, dimeric, and polymeric species may occur.

Copper(II) aromatic *N*-oxides have been studied extensively, not only because they form a variety of polynuclear species, but also because these complexes are paramagnetic and can be studied by electron paramagnetic resonance and by magnetic susceptibility methods. Recently, Watson (1969) summarized the magnetic properties of aromatic *N*-oxide copper(II) complexes in terms of 12 idealized structure types. Dimeric dibromobis(pyridine *N*-oxide)copper(II) has a magnetic moment which could not be interpreted on the assumption that this compound belongs to the same structure type as the chloride analog [dimeric dichlorobis(pyridine *N*-oxide)copper(II)]. A preliminary report (Mighell, Reimann & Santoro, 1970) shows that the structure of dimeric dibromobis(pyridine *N*-oxide) copper(II) differs markedly from that of the chloride complex, and does not fit the other structure types cited by Watson (1969). This paper reports the detailed structure of the bromide complex and its structural and magnetic properties in relation to those of closely related complexes.

Experimental

Single crystals of [(pyridine *N*-oxide)₂CuBr₂]₂ were kindly supplied by Dr R. W. Duerst. Laue symmetry

and approximate unit-cell parameters were determined from zero- and upper-level precession photographs. Precise unit-cell parameters were obtained by least-squares analysis using the 2θ angles of 37 reflections measured with a single-crystal diffractometer and Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The density of the complex was measured by the flotation method in a mixture of chloroform and tetrabromomethane. Crystal data are summarized in Table 1.

Table 1. *Crystal data*
for [(pyridine *N*-oxide)₂CuBr₂]₂

$a = 10.510$ (2) Å*	Space group = $P\bar{1}$
$b = 10.883$ (1)	$Z = 2$
$c = 11.818$ (5)	$\rho_o = 2.08$ g.cm ⁻³
$\alpha = 78.57$ (3)°	$\rho_c = 2.10$ g.cm ⁻³
$\beta = 89.88$ (3)	$V = 1309$ Å ³
$\gamma = 81.17$ (1)	

Linear absorption coefficient for Mo $K\alpha$; $\mu = 82$ cm⁻¹.

* Parameters are those of the reduced cell and were refined using 37 observed 2θ values.

The crystal used for intensity measurements was ground to a sphere of radius ~ 0.14 mm. Data were collected on a 3-circle diffractometer, with a take-off angle of approximately 4° and a scintillation counter and pulse-height analyzer set to admit 90% of the Mo $K\alpha$ radiation. All unique reflections with $2\theta \leq 60^\circ$ were measured by the scan method, using a scan rate of 2°/min and background settings calculated with the expression $2\theta \pm (\frac{1}{2})\Delta 2\theta$, where $\Delta 2\theta = 1.8 \times \tan \theta$ (Alexander & Smith, 1964). Also, six standard reflections were measured periodically to monitor radiation damage. The intensities of these standards decreased nearly linearly to $\sim 80\%$ of their initial values during data

Table 2. (a) Final atomic coordinates and anisotropic thermal parameters for [(pyridien *N*-oxide)₂CuBr₂]₂ and (b) calculated atomic coordinates for the hydrogen atoms.

(a)

The anisotropic temperature factor has the form;

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

Numbers in parentheses are standard deviations in the last significant digits.
Hydrogen atoms are labeled with the same numbers as the carbon atoms to which they are bonded.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.08498 (6)	0.03964 (7)	0.10254 (6)	45.3 (6)	65.4 (6)	36.1 (5)	-4.6 (5)	2.0 (4)	-17.9 (5)
Cu(2)	0.40118 (7)	0.57661 (7)	0.58753 (6)	57.2 (6)	66.2 (7)	40.3 (5)	-20.3 (5)	10.5 (5)	-18.4 (5)
Br(1)	0.00804 (6)	0.27311 (5)	0.08063 (6)	75.0 (6)	53.9 (5)	67.7 (5)	-11.3 (4)	9.0 (4)	-18.7 (4)
Br(2)	0.31186 (6)	-0.03640 (8)	0.12916 (6)	51.3 (5)	139.4 (9)	62.7 (5)	6.5 (5)	-3.4 (4)	-20.2 (6)
Br(3)	0.21565 (6)	0.47409 (7)	0.63258 (6)	79.1 (6)	94.2 (7)	68.1 (5)	-39.2 (5)	16.5 (5)	-17.4 (5)
Br(4)	0.43508 (7)	0.79740 (6)	0.52239 (6)	111.1 (7)	55.0 (5)	67.0 (5)	-19.9 (5)	5.2 (5)	-15.1 (4)
O(1)	0.0808 (3)	0.0427 (4)	-0.0651 (3)	42 (3)	97 (5)	41 (3)	-16 (3)	15 (3)	-13 (3)
N(1)	-0.1886 (4)	-0.0334 (5)	0.1295 (4)	39 (4)	74 (5)	39 (4)	-16 (3)	9 (3)	-27 (3)
C(11)	-0.2306 (6)	-0.1409 (6)	0.1818 (5)	68 (6)	69 (6)	63 (5)	-15 (5)	7 (4)	-13 (5)
C(12)	-0.3366 (7)	-0.1307 (7)	0.2490 (6)	89 (7)	89 (7)	64 (6)	-42 (6)	14 (5)	-6 (5)
C(13)	-0.3973 (6)	-0.0162 (7)	0.2652 (6)	56 (5)	117 (8)	56 (5)	-22 (5)	14 (4)	-22 (5)
C(14)	-0.3533 (6)	0.0939 (6)	0.2087 (6)	60 (5)	87 (6)	64 (5)	-11 (5)	12 (4)	-32 (5)
C(15)	-0.2478 (6)	0.0834 (6)	0.1391 (5)	61 (5)	71 (6)	57 (5)	-18 (4)	16 (4)	-27 (4)
O(2)	0.03817 (4)	-0.0095 (4)	0.2625 (3)	90 (5)	83 (4)	41 (3)	-31 (4)	2 (3)	-18 (3)
N(2)	0.0603 (5)	0.0619 (4)	0.3390 (4)	63 (4)	55 (4)	28 (3)	-15 (3)	0 (3)	-7 (3)
C(21)	-0.0390 (6)	0.1346 (7)	0.3760 (5)	80 (6)	90 (7)	46 (5)	4 (5)	-10 (4)	-4 (5)
C(22)	-0.0202 (8)	0.2030 (7)	0.4580 (6)	137 (9)	80 (7)	62 (6)	14 (6)	8 (6)	-18 (6)
C(23)	0.1015 (8)	0.1972 (7)	0.5030 (6)	149 (10)	71 (6)	60 (6)	-30 (6)	7 (6)	-23 (5)
C(24)	0.2022 (7)	0.1226 (7)	0.4633 (6)	99 (8)	111 (8)	59 (6)	-37 (6)	-12 (5)	-20 (6)
C(25)	0.1810 (6)	0.0521 (7)	0.3823 (6)	70 (6)	115 (8)	56 (5)	-27 (6)	-2 (4)	-33 (5)
O(3)	0.4102 (3)	0.5453 (4)	0.4284 (3)	39 (3)	95 (5)	48 (4)	-11 (3)	2 (3)	-29 (3)
N(3)	0.3011 (4)	0.5517 (5)	0.3634 (4)	46 (4)	63 (4)	36 (3)	-10 (3)	1 (3)	-2 (3)
C(31)	0.2672 (6)	0.4409 (6)	0.3475 (6)	80 (6)	65 (6)	57 (5)	-15 (5)	3 (4)	-2 (4)
C(32)	0.1601 (6)	0.4466 (6)	0.2790 (6)	85 (2)	89 (7)	60 (5)	-40 (5)	-2 (5)	-20 (5)
C(33)	0.0883 (6)	0.5619 (7)	0.2293 (6)	61 (6)	127 (8)	58 (5)	-23 (6)	-3 (4)	-14 (6)
C(34)	0.1284 (6)	0.6715 (7)	0.2491 (6)	74 (6)	83 (7)	80 (6)	-6 (5)	-7 (5)	-5 (5)
C(35)	0.2343 (6)	0.6645 (6)	0.3184 (6)	72 (6)	65 (6)	64 (5)	-10 (5)	2 (4)	-20 (5)
O(4)	0.5520 (5)	0.4132 (5)	0.2554 (4)	104 (5)	113 (5)	43 (3)	-53 (4)	18 (3)	-21 (4)
N(4)	0.5861 (5)	0.4982 (5)	0.1659 (4)	71 (5)	69 (5)	33 (4)	-29 (4)	15 (3)	-9 (3)
C(41)	0.5146 (7)	0.6122 (8)	0.1326 (6)	77 (7)	131 (9)	68 (6)	0 (6)	21 (5)	-18 (6)
C(42)	0.5477 (8)	0.6984 (8)	0.0409 (7)	105 (9)	109 (9)	90 (7)	7 (7)	6 (6)	0 (7)
C(43)	0.6569 (8)	0.6659 (7)	-0.0180 (7)	110 (8)	99 (8)	69 (9)	-22 (6)	18 (6)	-10 (6)
C(44)	0.7290 (7)	0.5492 (7)	0.0177 (7)	99 (8)	110 (8)	77 (6)	-21 (6)	40 (6)	-28 (6)
C(45)	0.6946 (6)	0.4665 (6)	0.1108 (6)	77 (6)	84 (7)	76 (6)	-7 (5)	26 (5)	-29 (5)

Table 2 (cont.)

(b)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(11)	0.808	0.775	0.170
H(12)	0.635	0.792	0.290
H(13)	0.530	0.992	0.319
H(14)	0.606	0.177	0.222
H(15)	0.779	0.161	0.099
H(21)	-0.127	0.144	0.344
H(22)	-0.095	0.255	0.485
H(23)	0.117	0.243	0.567
H(24)	0.290	0.118	0.492
H(25)	0.255	-0.002	0.356
H(31)	0.315	0.359	0.383
H(32)	0.137	0.367	0.262
H(33)	0.013	0.566	0.177
H(34)	0.082	0.753	0.210
H(35)	0.254	0.744	0.336
H(41)	0.436	0.633	0.172
H(42)	0.498	0.785	0.023
H(43)	0.677	0.728	-0.082
H(44)	0.806	0.525	-0.022
H(45)	0.753	0.387	0.141

collection. A total of 5458 reflections were measured; 1543 were considered unobserved. A reflection was

considered unobserved and assigned a value equal to twice the standard deviation, if the net number of counts did not exceed zero by at least twice the standard deviation. The intensities were corrected for Lorentz and polarization factors, for radiation damage, and for absorption (*International Tables for X-ray Crystallography* (1967); $\mu R = 1.17$).

Determination and refinement

All the atoms in the asymmetric unit, except hydrogen atoms, were located by Patterson and Fourier methods. The structure was then refined by block-diagonal least-squares analysis. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w^{\frac{1}{2}} = 1$ for $F_o < 70$ (absolute scale) and $w^{\frac{1}{2}} = 70/F_o$ for $F_o > 70$. Hydrogen atoms were included in the structure-factor calculations in fixed calculated positions (Santoro, Mighell, Zocchi & Reimann, 1969), with an isotropic temperature factor of 4.0 Å². After each refinement cycle, hydrogen-atom positions were recalculated from the refined ring carbon-atom posi-

Table 3. Observed and calculated structure factors

Columns are k , $10F_o$, $10F_c$ respectively. Unobserved reflections are marked with an (*).

Table with 10 columns: h, k, l, 10Fo, 10Fc, and 5 columns of phase angles. The table lists observed and calculated structure factors for various reflections, with unobserved ones marked with an asterisk.

Table 3 (cont.)

H=12.3		H=12.4		H=12.5		H=12.6		H=12.7		H=12.8		H=12.9		H=13.0	
h	k	l	F _o	h	k	l	F _o	h	k	l	F _o	h	k	l	F _o
1	100	66	8 565	-974	0	80	530	2	105	-77	0	655	628	0	374
2	100	36	8 562	235	2	105	-77	0	655	628	0	374			
3	100	6	8 559	-104	4	110	-70	0	652	625	0	371			
4	100	-36	8 556	110	6	115	-63	0	649	622	0	368			
5	100	-76	8 553	-118	8	120	-57	0	646	619	0	365			
6	100	-116	8 550	122	10	125	-51	0	643	616	0	362			
7	100	-156	8 547	-126	12	130	-45	0	640	613	0	359			
8	100	-196	8 544	130	14	135	-39	0	637	610	0	356			
9	100	-236	8 541	-134	16	140	-33	0	634	607	0	353			
10	100	-276	8 538	138	18	145	-27	0	631	604	0	350			
11	100	-316	8 535	-142	20	150	-21	0	628	601	0	347			
12	100	-356	8 532	146	22	155	-15	0	625	598	0	344			
13	100	-396	8 529	-150	24	160	-9	0	622	595	0	341			
14	100	-436	8 526	154	26	165	-3	0	619	592	0	338			
15	100	-476	8 523	-158	28	170	3	0	616	589	0	335			
16	100	-516	8 520	162	30	175	9	0	613	586	0	332			
17	100	-556	8 517	-166	32	180	15	0	610	583	0	329			
18	100	-596	8 514	170	34	185	21	0	607	580	0	326			
19	100	-636	8 511	-174	36	190	27	0	604	577	0	323			
20	100	-676	8 508	178	38	195	33	0	601	574	0	320			
21	100	-716	8 505	-182	40	200	39	0	598	571	0	317			
22	100	-756	8 502	186	42	205	45	0	595	568	0	314			
23	100	-796	8 499	-190	44	210	51	0	592	565	0	311			
24	100	-836	8 496	194	46	215	57	0	589	562	0	308			
25	100	-876	8 493	-198	48	220	63	0	586	559	0	305			
26	100	-916	8 490	202	50	225	69	0	583	556	0	302			
27	100	-956	8 487	-206	52	230	75	0	580	553	0	299			
28	100	-996	8 484	210	54	235	81	0	577	550	0	296			
29	100	-1036	8 481	-214	56	240	87	0	574	547	0	293			
30	100	-1076	8 478	218	58	245	93	0	571	544	0	290			
31	100	-1116	8 475	-222	60	250	99	0	568	541	0	287			
32	100	-1156	8 472	226	62	255	105	0	565	538	0	284			
33	100	-1196	8 469	-230	64	260	111	0	562	535	0	281			
34	100	-1236	8 466	234	66	265	117	0	559	532	0	278			
35	100	-1276	8 463	-238	68	270	123	0	556	529	0	275			
36	100	-1316	8 460	242	70	275	129	0	553	526	0	272			
37	100	-1356	8 457	-246	72	280	135	0	550	523	0	269			
38	100	-1396	8 454	250	74	285	141	0	547	520	0	266			
39	100	-1436	8 451	-254	76	290	147	0	544	517	0	263			
40	100	-1476	8 448	258	78	295	153	0	541	514	0	260			
41	100	-1516	8 445	-262	80	300	159	0	538	511	0	257			
42	100	-1556	8 442	266	82	305	165	0	535	508	0	254			
43	100	-1596	8 439	-270	84	310	171	0	532	505	0	251			
44	100	-1636	8 436	274	86	315	177	0	529	502	0	248			
45	100	-1676	8 433	-278	88	320	183	0	526	499	0	245			
46	100	-1716	8 430	282	90	325	189	0	523	496	0	242			
47	100	-1756	8 427	-286	92	330	195	0	520	493	0	239			
48	100	-1796	8 424	290	94	335	201	0	517	490	0	236			
49	100	-1836	8 421	-294	96	340	207	0	514	487	0	233			
50	100	-1876	8 418	298	98	345	213	0	511	484	0	230			
51	100	-1916	8 415	-302	100	350	219	0	508	481	0	227			
52	100	-1956	8 412	306	102	355	225	0	505	478	0	224			
53	100	-1996	8 409	-310	104	360	231	0	502	475	0	221			
54	100	-2036	8 406	314	106	365	237	0	499	472	0	218			
55	100	-2076	8 403	-318	108	370	243	0	496	469	0	215			
56	100	-2116	8 400	322	110	375	249	0	493	466	0	212			
57	100	-2156	8 397	-326	112	380	255	0	490	463	0	209			
58	100	-2196	8 394	330	114	385	261	0	487	460	0	206			
59	100	-2236	8 391	-334	116	390	267	0	484	457	0	203			
60	100	-2276	8 388	338	118	395	273	0	481	454	0	200			
61	100	-2316	8 385	-342	120	400	279	0	478	451	0	197			
62	100	-2356	8 382	346	122	405	285	0	475	448	0	194			
63	100	-2396	8 379	-350	124	410	291	0	472	445	0	191			
64	100	-2436	8 376	354	126	415	297	0	469	442	0	188			
65	100	-2476	8 373	-358	128	420	303	0	466	439	0	185			
66	100	-2516	8 370	362	130	425	309	0	463	436	0	182			
67	100	-2556	8 367	-366	132	430	315	0	460	433	0	179			
68	100	-2596	8 364	370	134	435	321	0	457	430	0	176			
69	100	-2636	8 361	-374	136	440	327	0	454	427	0	173			
70	100	-2676	8 358	378	138	445	333	0	451	424	0	170			
71	100	-2716	8 355	-382	140	450	339	0	448	421	0	167			
72	100	-2756	8 352	386	142	455	345	0	445	418	0	164			
73	100	-2796	8 349	-390	144	460	351	0	442	415	0	161			
74	100	-2836	8 346	394	146	465	357	0	439	412	0	158			
75	100	-2876	8 343	-398	148	470	363	0	436	409	0	155			
76	100	-2916	8 340	402	150	475	369	0	433	406	0	152			
77	100	-2956	8 337	-406	152	480	375	0	430	403	0	149			
78	100	-2996	8 334	410	154	485	381	0	427	400	0	146			
79	100	-3036	8 331	-414	156	490	387	0	424	397	0	143			
80	100	-3076	8 328	418	158	495	393	0	421	394	0	140			
81	100	-3116	8 325	-422	160	500	399	0	418	391	0	137			
82	100	-3156	8 322	426	162	505	405	0	415	388	0	134			
83	100	-3196	8 319	-426	164	510	411	0	412	385	0	131			
84	100	-3236	8 316	430	166	515	417	0	409	382	0	128			
85	100	-3276	8 313	-430	168	520	423	0	406	379	0	125			
86	100	-3316	8 310	434	170	525	429	0	403	376	0	122			
87	100	-3356	8 307	-434	172	530	435	0	400	373	0	119			
88	100	-3396	8 304	438	174	535	441	0	397	370	0	116			
89	100	-3436	8 301	-438	176	540	447	0	394	367	0	113			
90	100	-3476	8 298	442	178	545	453	0	391	364	0	110			
91	100	-3516	8 295	-442	180	550	459	0	388	361	0	107			
92	100	-3556	8 292	446	182	555	465	0	385	358	0	104			
93	100	-3596	8 289	-446	184	560	471	0	382	355	0	101			
94	100	-3636	8 286	450	186	565	477	0	379	352	0	98			
95	100	-3676	8 283	-450	188	570	483	0	376	349	0	95			
96	100	-3716	8 280	454	190	575	489	0	373	346	0	92			
97	100	-3756	8 277	-454	192	580	495	0	370	343	0	89			
98	100	-3796	8 274	458	194	585	501	0	367	340	0	86			
99	100	-3836	8 271	-458	196	590	507	0	364	337	0	83			
100	100	-3876	8 268	462	198	595	513	0	361	334	0	80			

tions. Scattering factors for neutral copper, bromine, X-ray Crystallography (1962). The F_0 's of 'unobserved' nitrogen, carbon, and for singly negative reflections were weighted zero or one, depending on oxygen atoms were taken from *International Tables for* whether corresponding F_c 's were less or greater than

Table 3 (cont.)

H ₂ 3/8	119	378	356	-1 117	127	1 267	134	8 188	-145	-7 107	98	2 330	-336	-5 353	-352	3 09	-150	-7 550	-552	H ₂ 9/12	-8	90	52	H ₂ 11/13	-4	90	52	H ₂ 12/13	-4	90	52	H ₂ 13/14	-4	90	52	H ₂ 14/15	-4	90	52	H ₂ 15/16	-4	90	52	H ₂ 16/17	-4	90	52	H ₂ 17/18	-4	90	52	H ₂ 18/19	-4	90	52	H ₂ 19/20	-4	90	52	H ₂ 20/21	-4	90	52	H ₂ 21/22	-4	90	52	H ₂ 22/23	-4	90	52	H ₂ 23/24	-4	90	52	H ₂ 24/25	-4	90	52	H ₂ 25/26	-4	90	52	H ₂ 26/27	-4	90	52	H ₂ 27/28	-4	90	52	H ₂ 28/29	-4	90	52	H ₂ 29/30	-4	90	52	H ₂ 30/31	-4	90	52	H ₂ 31/32	-4	90	52	H ₂ 32/33	-4	90	52	H ₂ 33/34	-4	90	52	H ₂ 34/35	-4	90	52	H ₂ 35/36	-4	90	52	H ₂ 36/37	-4	90	52	H ₂ 37/38	-4	90	52	H ₂ 38/39	-4	90	52	H ₂ 39/40	-4	90	52	H ₂ 40/41	-4	90	52	H ₂ 41/42	-4	90	52	H ₂ 42/43	-4	90	52	H ₂ 43/44	-4	90	52	H ₂ 44/45	-4	90	52	H ₂ 45/46	-4	90	52	H ₂ 46/47	-4	90	52	H ₂ 47/48	-4	90	52	H ₂ 48/49	-4	90	52	H ₂ 49/50	-4	90	52	H ₂ 50/51	-4	90	52	H ₂ 51/52	-4	90	52	H ₂ 52/53	-4	90	52	H ₂ 53/54	-4	90	52	H ₂ 54/55	-4	90	52	H ₂ 55/56	-4	90	52	H ₂ 56/57	-4	90	52	H ₂ 57/58	-4	90	52	H ₂ 58/59	-4	90	52	H ₂ 59/60	-4	90	52	H ₂ 60/61	-4	90	52	H ₂ 61/62	-4	90	52	H ₂ 62/63	-4	90	52	H ₂ 63/64	-4	90	52	H ₂ 64/65	-4	90	52	H ₂ 65/66	-4	90	52	H ₂ 66/67	-4	90	52	H ₂ 67/68	-4	90	52	H ₂ 68/69	-4	90	52	H ₂ 69/70	-4	90	52	H ₂ 70/71	-4	90	52	H ₂ 71/72	-4	90	52	H ₂ 72/73	-4	90	52	H ₂ 73/74	-4	90	52	H ₂ 74/75	-4	90	52	H ₂ 75/76	-4	90	52	H ₂ 76/77	-4	90	52	H ₂ 77/78	-4	90	52	H ₂ 78/79	-4	90	52	H ₂ 79/80	-4	90	52	H ₂ 80/81	-4	90	52	H ₂ 81/82	-4	90	52	H ₂ 82/83	-4	90	52	H ₂ 83/84	-4	90	52	H ₂ 84/85	-4	90	52	H ₂ 85/86	-4	90	52	H ₂ 86/87	-4	90	52	H ₂ 87/88	-4	90	52	H ₂ 88/89	-4	90	52	H ₂ 89/90	-4	90	52	H ₂ 90/91	-4	90	52	H ₂ 91/92	-4	90	52	H ₂ 92/93	-4	90	52	H ₂ 93/94	-4	90	52	H ₂ 94/95	-4	90	52	H ₂ 95/96	-4	90	52	H ₂ 96/97	-4	90	52	H ₂ 97/98	-4	90	52	H ₂ 98/99	-4	90	52	H ₂ 99/100	-4	90	52	H ₂ 100/101	-4	90	52	H ₂ 101/102	-4	90	52	H ₂ 102/103	-4	90	52	H ₂ 103/104	-4	90	52	H ₂ 104/105	-4	90	52	H ₂ 105/106	-4	90	52	H ₂ 106/107	-4	90	52	H ₂ 107/108	-4	90	52	H ₂ 108/109	-4	90	52	H ₂ 109/110	-4	90	52	H ₂ 110/111	-4	90	52	H ₂ 111/112	-4	90	52	H ₂ 112/113	-4	90	52	H ₂ 113/114	-4	90	52	H ₂ 114/115	-4	90	52	H ₂ 115/116	-4	90	52	H ₂ 116/117	-4	90	52	H ₂ 117/118	-4	90	52	H ₂ 118/119	-4	90	52	H ₂ 119/120	-4	90	52	H ₂ 120/121	-4	90	52	H ₂ 121/122	-4	90	52	H ₂ 122/123	-4	90	52	H ₂ 123/124	-4	90	52	H ₂ 124/125	-4	90	52	H ₂ 125/126	-4	90	52	H ₂ 126/127	-4	90	52	H ₂ 127/128	-4	90	52	H ₂ 128/129	-4	90	52	H ₂ 129/130	-4	90	52	H ₂ 130/131	-4	90	52	H ₂ 131/132	-4	90	52	H ₂ 132/133	-4	90	52	H ₂ 133/134	-4	90	52	H ₂ 134/135	-4	90	52	H ₂ 135/136	-4	90	52	H ₂ 136/137	-4	90	52	H ₂ 137/138	-4	90	52	H ₂ 138/139	-4	90	52	H ₂ 139/140	-4	90	52	H ₂ 140/141	-4	90	52	H ₂ 141/142	-4	90	52	H ₂ 142/143	-4	90	52	H ₂ 143/144	-4	90	52	H ₂ 144/145	-4	90	52	H ₂ 145/146	-4	90	52	H ₂ 146/147	-4	90	52	H ₂ 147/148	-4	90	52	H ₂ 148/149	-4	90	52	H ₂ 149/150	-4	90	52	H ₂ 150/151	-4	90	52	H ₂ 151/152	-4	90	52	H ₂ 152/153	-4	90	52	H ₂ 153/154	-4	90	52	H ₂ 154/155	-4	90	52	H ₂ 155/156	-4	90	52	H ₂ 156/157	-4	90	52	H ₂ 157/158	-4	90	52	H ₂ 158/159	-4	90	52	H ₂ 159/160	-4	90	52	H ₂ 160/161	-4	90	52	H ₂ 161/162	-4	90	52	H ₂ 162/163	-4	90	52	H ₂ 163/164	-4	90	52	H ₂ 164/165	-4	90	52	H ₂ 165/166	-4	90	52	H ₂ 166/167	-4	90	52	H ₂ 167/168	-4	90	52	H ₂ 168/169	-4	90	52	H ₂ 169/170	-4	90	52	H ₂ 170/171	-4	90	52	H ₂ 171/172	-4	90	52	H ₂ 172/173	-4	90	52	H ₂ 173/174	-4	90	52	H ₂ 174/175	-4	90	52	H ₂ 175/176	-4	90	52	H ₂ 176/177	-4	90	52	H ₂ 177/178	-4	90	52	H ₂ 178/179	-4	90	52	H ₂ 179/180	-4	90	52	H ₂ 180/181	-4	90	52	H ₂ 181/182	-4	90	52	H ₂ 182/183	-4	90	52	H ₂ 183/184	-4	90	52	H ₂ 184/185	-4	90	52	H ₂ 185/186	-4	90	52	H ₂ 186/187	-4	90	52	H ₂ 187/188	-4	90	52	H ₂ 188/189	-4	90	52	H ₂ 189/190	-4	90	52	H ₂ 190/191	-4	90	52	H ₂ 191/192	-4	90	52	H ₂ 192/193	-4	90	52	H ₂ 193/194	-4	90	52	H ₂ 194/195	-4	90	52	H ₂ 195/196	-4	90	52	H ₂ 196/197	-4	90	52	H ₂ 197/198	-4	90	52	H ₂ 198/199	-4	90	52	H ₂ 199/200	-4	90	52	H ₂ 200/201	-4	90	52	H ₂ 201/202	-4	90	52	H ₂ 202/203	-4	90	52	H ₂ 203/204	-4	90	52	H ₂ 204/205	-4	90	52	H ₂ 205/206	-4	90	52	H ₂ 206/207	-4	90	52	H ₂ 207/208	-4	90	52	H ₂ 208/209	-4	90	52	H ₂ 209/210	-4	90	52	H ₂ 210/211	-4	90	52	H ₂ 211/212	-4	90	52	H ₂ 212/213	-4	90	52	H ₂ 213/214	-4	90	52	H ₂ 214/215	-4	90	52	H ₂ 215/216	-4	90	52	H ₂ 216/217	-4	90	52	H ₂ 217/218	-4	90	52	H ₂ 218/219	-4	90	52	H ₂ 219/220	-4	90	52	H ₂ 220/221	-4	90	52	H ₂ 221/222	-4	90	52	H ₂ 222/223	-4	90	52	H ₂ 223/224	-4	90	52	H ₂ 224/225	-4	90	52	H ₂ 225/226	-4	90	52	H ₂ 226/227	-4	90	52	H ₂ 227/228	-4	90	52	H ₂ 228/229	-4	90	52	H ₂ 229/230	-4	90	52	H ₂ 230/231	-4	90	52	H ₂ 231/232	-4	90	52	H ₂ 232/233	-4	90	52	H ₂ 233/234	-4	90	52	H ₂ 234/235	-4	90	52	H ₂ 235/236	-4	90	52	H ₂ 236/237	-4	90	52	H ₂ 237/238	-4	90	52	H ₂ 238/239	-4	90	52	H ₂ 239/240	-4	90	52	H ₂ 240/241	-4	90	52	H ₂ 241/242	-4	90	52	H ₂ 242/243	-4	90	52	H ₂ 243/244	-4	90	52	H ₂ 244/245	-4	90	52	H ₂ 245/246	-4	90	52	H ₂ 246/247	-4	90	52	H ₂ 247/248	-4	90	52	H ₂ 248/249	-4	90	52	H ₂ 249/250	-4	90	52	H ₂ 250/251	-4	90	52	H ₂ 251/252	-4	90	52	H ₂ 252/253	-4	90	52	H ₂ 253/254	-4	90	52	H ₂ 254/255	-4	90	52	H ₂ 255/256	-4	90	52	H ₂ 256/257	-4	90	52	H ₂ 257/258	-4	90	52	H ₂ 258/259	-4	90	52	H ₂ 259/260	-4	90	52	H ₂ 260/261	-4	90	52	H ₂ 261/262	-4	90	52	H ₂ 262/263	-4	90	52	H ₂ 263/264	-4	90	52	H ₂ 264/265	-4	90	52	H ₂ 265/266	-4	90	52	H ₂ 266/267	-4	90	52	H ₂ 267/268	-4	90	52	H ₂ 268/269	-4	90	52	H ₂ 269/270	-4	90	52	H ₂ 270/271	-4	90	52	H ₂ 271/272	-4	90	52	H ₂ 272/273	-4	90	52	H ₂ 273/274	-4	90	52	H ₂ 274/275	-4	90	52	H ₂ 275/276	-4	90	52	H ₂ 276/277	-4	90	52	H ₂ 277/278	-4	90	52	H ₂ 278/279	-4	90	52	H ₂ 279/280	-4	90	52	H ₂ 280/281	-4	90	52	H ₂ 281/282	-4	90	52	H ₂ 282/283	-4	90	52	H ₂ 283/284	-4	90	52	H ₂ 284/285	-4	90	52	H ₂ 285/286	-4	90	52	H ₂ 286/287	-4	90	52	H ₂ 287/288	-4	90	52	H ₂ 288/289	-4	90	52	H ₂ 289/290	-4	90	52	H ₂ 290/291	-4	90	52	H ₂ 291/292	-4	90	52	H ₂ 292/293	-4	90	52	H ₂ 293/294	-4	
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atom, and by two bromine atoms. Bond distances and angles for the two dimers are given in Table 4 and in Fig. 4.

A comparison between Figs. 2 and 3 and the data given in Table 4 shows that the two dimers, though similar, differ in some important details. Differences are observed in the configuration of the bridging planes,

in the $\text{Cu} \begin{smallmatrix} \text{Br} \\ \text{Br} \end{smallmatrix}$ groups, and in the orientation of the rings relative to the bridging parallelogram. The short Cu-O distances in the two dimers agree to within one standard deviation, but the long Cu-O bond is 0.08 \AA (20σ) greater in dimer II than in dimer I. Consequently the Cu-Cu distance is longer in dimer II, as the angles

Table 4. *Coordination polyhedra about copper**

Polyhedron about Cu(1)		Polyhedron about Cu(2)	
Cu(1)-O(1)	1.975 (4) Å	Cu(2)-O(31)	1.976 (4) Å
Cu(1)-O(1')	2.162 (4)	Cu(2)-O(31')	2.240 (4)
Cu(1)-O(21)	1.944 (4)	Cu(2)-O(41)	1.949 (4)
Cu(1)-Br(1)	2.507 (1)	Cu(2)-Br(3)	2.400 (1)
Cu(1)-Br(2)	2.401 (1)	Cu(2)-Br(4)	2.454 (1)
Br(1)-Cu(1)-Br(2)	118.60 (4)°	Br(3)-Cu(2)-Br(4)	134.65 (4)°
Br(1)-Cu(1)-O(1)	106.03 (11)	Br(3)-Cu(2)-O(31)	94.01 (12)
Br(1)-Cu(1)-O(1')	94.45 (12)	Br(3)-Cu(2)-O(31')	118.01 (12)
Br(1)-Cu(1)-O(21)	97.06 (14)	Br(3)-Cu(2)-O(41)	97.59 (15)
Br(2)-Cu(1)-O(1)	134.61 (11)	Br(4)-Cu(2)-O(31)	91.96 (13)
Br(2)-Cu(1)-O(1')	95.09 (11)	Br(4)-Cu(2)-O(31')	106.58 (11)
Br(2)-Cu(1)-O(21)	97.43 (13)	Br(4)-Cu(2)-O(41)	89.20 (15)
O(1)-Cu(1)-O(1')	72.60 (16)	O(31)-Cu(2)-O(31')	71.99 (15)
O(1)-Cu(1)-O(21)	84.34 (18)	O(31)-Cu(2)-O(41)	162.48 (17)
O(21)-Cu(1)-O(1')	156.33 (19)	O(41)-Cu(2)-O(41)	90.93 (17)

* Cu(1)-Cu(1'): 3.336 (1) Å

Cu(2)-Cu(2)': 3.415 (1) Å.

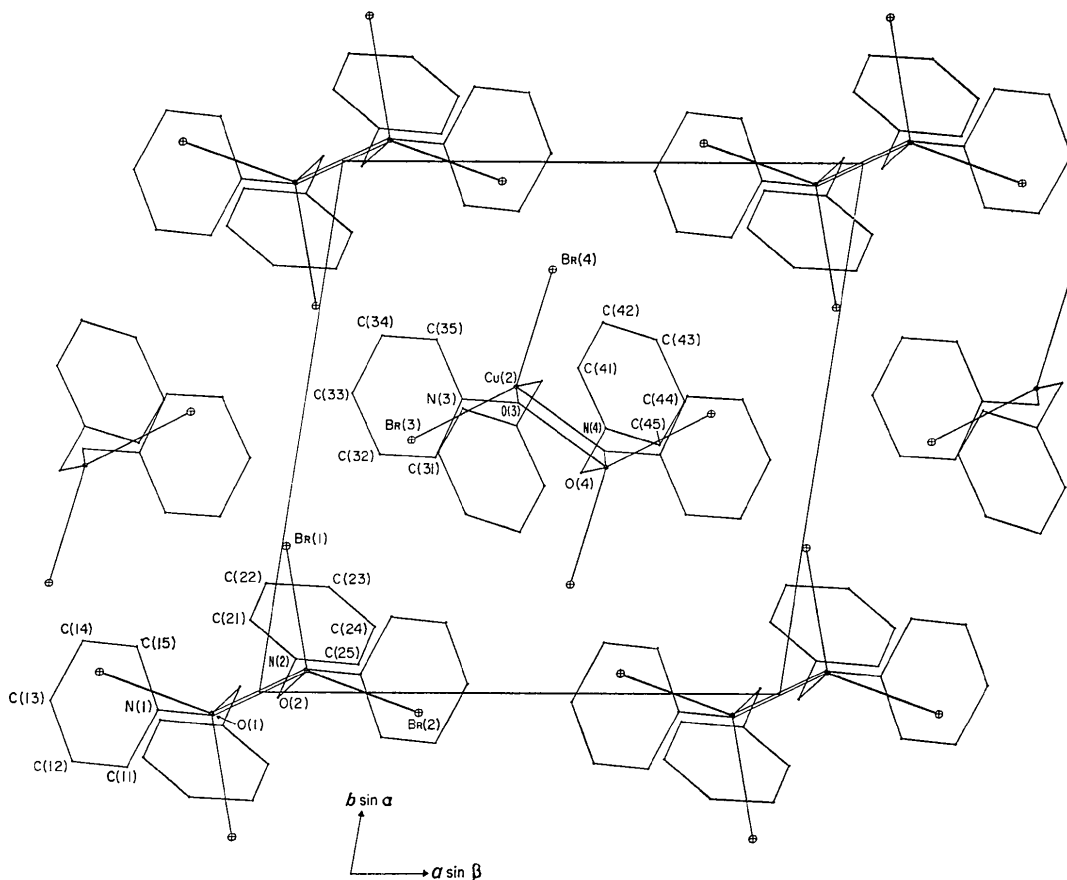


Fig. 1. Projection of $[(\text{pyridine } N\text{-oxide})_2\text{CuBr}_2]_2$ down the c axis.

O(1)–Cu(1)–O(1') and O(3)–Cu(2)–O(3') are equal to within 3σ . The bromine atoms of the CuBr₂ groups lie above and below the bridging plane in both dimers, but they are more nearly equidistant from this plane in dimer II (2.11 and 2.35 Å) than in dimer I (2.41 and 1.68 Å).

The Cu \angle Br angle is 16.1° larger, and the Cu–Br bond distances are more nearly equal in dimer II than in dimer I. Pyridine rings of the pyridine *N*-oxide molecules were found by least-squares analysis to be planar to within experimental error (Table 5). The orientation of the bridging pyridine *N*-oxide molecules with respect to the bridging plane does not differ appreciably in the two dimers (compare Figs. 2 and 3), but the orientation of the non-bridging molecules is considerably different. To bring the non-bridging pyridine ring in dimer II into an orientation approximately equivalent to that assumed by the corresponding ring in dimer I would require a rotation of the ring of $\sim 60^\circ$ about the Cu(2)–O(4) bond. For all four independent pyridine rings, deviations of the oxygen atoms from the planes of the

rings are much larger than the mean deviation of the carbon and nitrogen atoms. Observed N–O distances are longer when the oxygen atom is bridging than when it is non-bridging (1.366 *vs.* 1.346 Å). This difference is only about 3σ , but the fact that the infrared spectrum shows two N–O stretching frequencies (Muto & Jonassen, 1966) indicates that it is real.

Discussion

The magnetic properties of more than 100 aromatic *N*-oxide copper(II) complexes have been summarized recently by Watson (1969) in an effort to generalize their magnetic behavior in terms of 12 idealized structure types. Dimeric dibromobis(pyridine *N*-oxide)-copper(II) was cited as probably belonging to the same structure type as the chloride analog and as having a larger magnetic moment than the chloride analog. This result was unexpected, for in the 1:1 series of pyridine *N*-oxide complexes bromides exhibit smaller room-temperature moments.

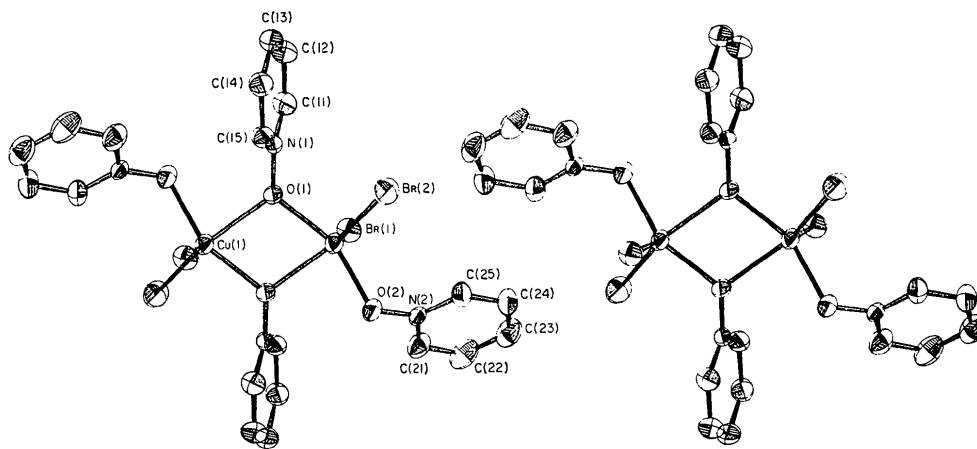


Fig. 2. Stereo view of dimer I. This figure (as well as Fig. 3) is drawn so that the bridging plane (defined by a copper atom and two bridging oxygen atoms) is in the plane of the paper.

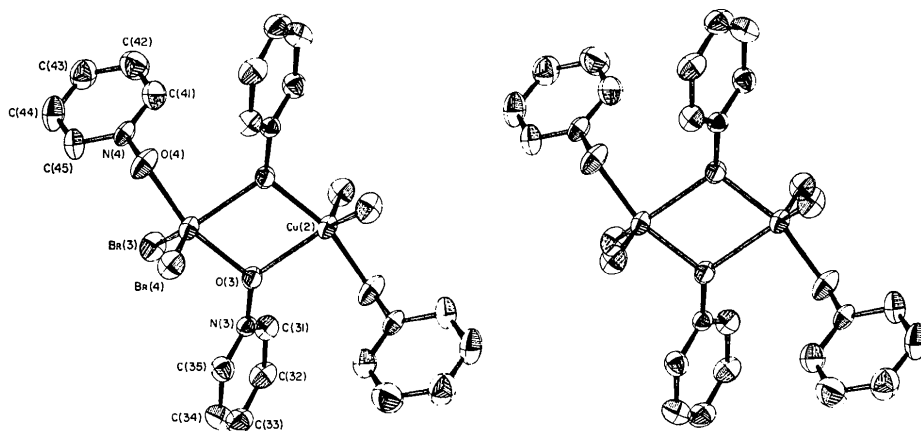


Fig. 3. Stereo view of dimer II.

The results reported here show that the structures of the bromide and chloride (Morrow, 1965) complexes differ significantly, even though the structural unit is a pentacoordinated dimer and the copper-copper dis-

tances are about the same in both cases. The principal difference between the two complexes is in the orientation of the bridging plane with respect to the Cu(halogen)₂ groups. In the chloride dimer the chlorine, copper, and bridging oxygen atoms lie approximately in a plane, and the non-bridging oxygen atoms lie above and below this plane. For the bromide dimer to fit the structure type of the chloride dimer, the plane of the copper and bridging oxygen atoms would have to be rotated $\sim 90^\circ$ with respect to the rest of the structure. This large difference shows that the bromide structure is not a minor variant of the chloride structure. The closest structural comparison can be made with the unsymmetrically bridged [(pyridine *N*-oxide)₂Cu(NO₃)₂]₂ (Ščavničar & Matković, 1969). In the nitrate dimer, the coordination sphere about each copper atom is approximately a pyramid with a square base. The coordination in the base consists of two *trans* monodentate nitrate groups, a non-bridging oxygen atom, and a bridging oxygen atom. The square bases are connected by the long sides of the unsymmetrical bridges such that the bridging oxygen atom serves as a basal site for one copper atom and as an apical site for the other. In order for the bromide complex to fit the structure of the nitrate complex, the long side of the unsymmetrical bridge would have to be increased ~ 0.2 Å and the Cu-Br angles would have to be increased $\sim 50^\circ$.

The magnetic moment of the bromide complex (1.4, Gruber, Harris, Kokot, Lenzer, Lockyer & Sinn, 1967) is intermediate between the value reported for the nitrate complex (1.88, Whymann & Hatfield, 1967) and the values reported for the chloride complex (0.46, Gruber *et al.*, 1967; and 0.63, Kato, Jonassen & Fanning, 1964). The difference in the magnetic moments of the latter two compounds is ascribed (Watson, 1969) to a different spatial relationship between adjacent interacting orbitals. Specifically, Watson assumes that the unpaired electrons in both dimers occupy primarily $d_{x^2-y^2}$ orbitals, which are localized in the square bases about the copper ions. Because of the structural dif-

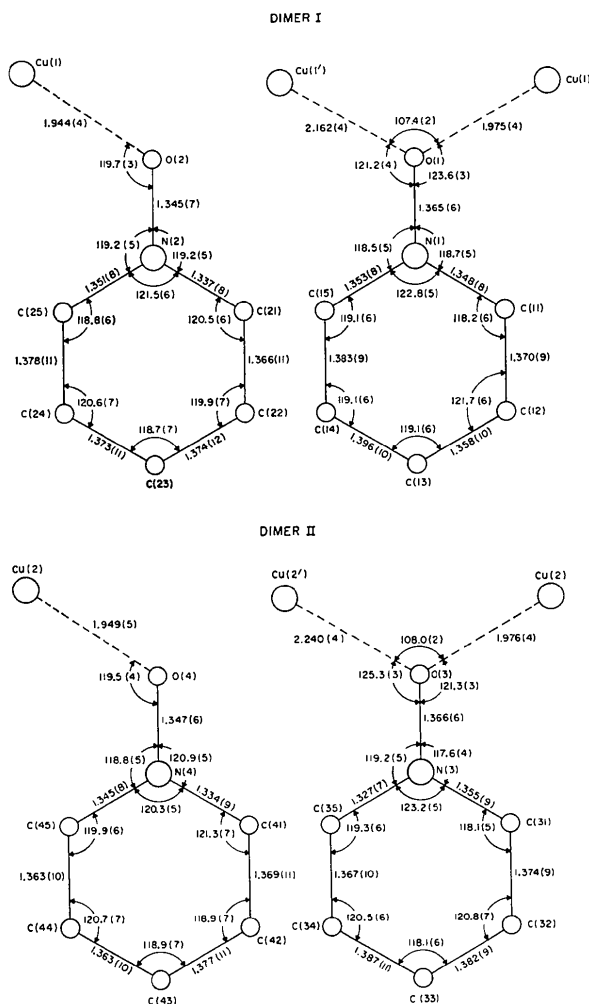


Fig. 4. Bond angles and distances for the coordinated pyridine *N*-oxide rings in dimer I and dimer II.

Table 5. Distances from the least-squares plane* calculated through the six ring atoms of the pyridine ring in the pyridine *N*-oxide ligand

	Dimer I		Dimer II				
	Ring 1	Ring 2	Ring 3	Ring 4			
N(11)	0.012 Å	N(21)	0.007 Å	N(31)	-0.007 Å	N(41)	-0.010 Å
C(11)	0.001	C(21)	0.001	C(31)	0.003	C(41)	0.000
C(12)	-0.013	C(22)	-0.003	C(32)	-0.001	C(42)	0.007
C(13)	0.012	C(23)	-0.003	C(33)	0.004	C(43)	-0.004
C(14)	0.001	C(24)	0.011	C(34)	-0.008	C(44)	-0.007
C(15)	-0.013	C(25)	-0.013	C(35)	0.010	C(45)	0.014
O(1)	0.065	O(21)	-0.058	O(31)	-0.050	O(41)	-0.033

* Equation of the plane in direct space is:

$$PX + QY + RZ = S$$

1st ring:	P = 6.324	Q = 2.223	R = 9.437	S = 8.490
2nd ring:	P = 2.876	Q = 7.318	R = -6.818	S = -1.692
3rd ring:	P = -6.088	Q = 3.889	R = 9.609	S = 1.881
4th ring:	P = 6.338	Q = 6.495	R = 8.321	S = 8.341

ferences, the pair of copper $d_{x^2-y^2}$ orbitals are coplanar in the chloride complex and are 'stacked' in a pair of parallel planes in the nitrate complex. In the chloride dimer, the $d_{x^2-y^2}$ orbitals share an edge (two oxygen atoms), and the overlap is larger than in the nitrate dimer. Consequently, the spin-pairing interactions are larger in the chloride dimer and the room-temperature magnetic moment is smaller than that of the nitrate.

Because of the low-symmetry environment (C_1) about the copper(II) ion in the bromide complex, an orbital description as simple as that invoked in the other two compounds cannot be given. A relationship between the magnetic properties of the bromide, chloride, and nitrate complexes can be developed indirectly by showing that the configuration of the bromide dimers is intermediate between two hypothetical structures for which it is possible to give a simple orbital description. In a fivefold coordinated copper complex, the environment about the copper atom is generally a distorted one with relatively strong bonding to four atoms in a plane (XY), and weaker bonding to the fifth atom in a Z direction roughly perpendicular to the (XY) plane (Muetterties & Schunn, 1966). The two hypothetical structures can be postulated on the basis of two different directions of the weak bonding.

In the first case, the weak bond in the Z direction is a Cu-Br bond. The bridge connecting the two copper atoms is assumed to be symmetrical with short (~ 2.0 Å) Cu-O bonds. The non-bridging oxygen atom is also tightly bound and is coplanar with the bridging parallelogram. The fourth bond in the (XY) plane is a Cu-Br bond shorter than the one in the Z direction. In this idealized structure, the copper $d_{x^2-y^2}$ orbitals would be coplanar and would share two tightly bound oxygen atoms. From the standpoint of the relationship between the copper orbitals, this case would be the same as that in dimeric dichlorobis(pyridine *N*-oxide)copper(II).

In the second case, the weak bond in the Z direction is one between the copper atom and one of the bridging oxygen atoms. Therefore, the bridge between copper atoms is unsymmetrical with one Cu-O bond distance of ~ 2.0 Å. The (XY) plane contains two oxygen atoms *trans* to one another and two bromine atoms also *trans* to one another. From the standpoint of both the structure and the relationship between copper orbitals, this case is the same as in $[(\text{pyridine } N\text{-oxide})_2\text{Cu}(\text{NO}_3)_2]_2$.

In comparing observed structural features of the bromide dimers with those of the limiting cases, we note that the bridging parallelogram is more symmetrical in dimer I than in dimer II. Consequently, dimer I should more closely resemble the first idealized structure, and dimer II the second. Table 4 and Fig. 4 show that this is actually observed, e.g. in dimer I the Cu-Br bond distances differ by 0.1 Å and the bromine atom closest to the copper atom lies more nearly in the plane of the three oxygen atoms. In dimer II the Cu-Br bond

distances are more nearly equivalent, and the Cu-Br angle has opened 16° toward a *trans* configuration. This analysis, which assumes that the bridge, Cu-Br bond distances, and Cu-Br angles are related quantities, shows that the observed structure may be viewed as two points on a continuum between the two idealized structures. As the relationship between copper orbitals in the two postulated structures resemble the relationship postulated for the chloride and nitrate dimers respectively, the intermediate magnetic moment of the bromide complex would appear to be a consequence of its intermediate structure type. In any case, the two crystallographically non-equivalent dimers are probably different enough to require two separate J values to describe the temperature dependence of the magnetic susceptibility.

Computer calculations were made with local programs, with the *Program System for X-ray Crystallography* (1967), and with the *ORTEP* plotting program (Johnson, 1965).

References

- ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.
- GRUBER, S. J., HARRIS, C. M., KOKOT, E., LENZER, S. L., LOCKYER, T. N. & SINN, E. (1967). *Austral. J. Chem.* **20**, 2403.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201-207, Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1967). Vol. II, pp. 302-305, Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP: A Fortran Thermal-Ellipsoid Program for Crystal Structure Illustrations*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KATO, M., JONASSEN, H. B. & FANNING, J. C. (1964). *Chem. Rev.* **64**, 99.
- MIGHELL, A. D., REIMANN, C. W. & SANTORO, A. (1970). *Chem. Commun.* **4**, 204.
- MORROW, J. C. (1965). *Abstracts American Crystallographic Association*, p. 34. Gatlinburg, Tennessee.
- MUETTERTIES, E. L. & SCHUNN, R. A. (1966). *Quart. Rev.* **20**, 245.
- MUTO, Y. & JONASSEN, H. B. (1966). *Bull. Chem. Soc. Japan*, **39**, 58.
- ORCHIN, M. & SCHMIDT, P. J. (1968). *Coordin. Chem. Rev.* **3**, 345.
- Program System for X-ray Crystallography* (1967). Developed at Univ. of Maryland in collaboration with Natl. Bureau of Standards and the Geological Survey.
- SANTORO, A., MIGHELL, A. D., ZOCCHI, M. & REIMANN, C. W. (1969). *Acta Cryst.* **B25**, 842.
- ŠČAVNIČAR, S. & MATKOVIĆ, B. (1969). *Acta Cryst.* **B25**, 2046.
- WATSON, W. H. (1969). *Inorg. Chem.* **8**, 1879.
- WHYMAN, R. & HATFIELD, W. F. (1967). *Inorg. Chem.* **6**, 1859.