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Magnetic Interaction in Binuclear Copper(II) Complexes: Preparation and Structure of the Schiff Base Complex Derived From Pyrrole-2-Carboxaldehyde and 3-Aminopropanol

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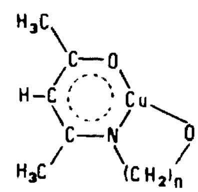
To obtain additional information about the relationship between magnetic properties and structure in oxygen-bridged complexes, the copper(II) complex of the Schiff base of pyrrole-2-carboxaldehyde and 3-aminopropanol was prepared. The complex, $[Cu(C_8H_{10}N_2O)]_2$*, crystallizes as monoclinic crystals* ($a = 25.61$ Å, $b = 5.46$ Å, $c = 16.90$ Å, $\beta = 136.33°$) *of space group C2/c with 8 formula units (4 dimers) per unit cell* ($\rho_{obsd} = 1.73$, $\rho_{calcd} = 1.74$ g/cm^3). *A total of 858 unique, non-zero reflections were obtained from precession camera photographs; the structure was solved from Patterson and electron density maps and refined by least-squares methods to a ocnventional R value of 0.076. The coordination of copper is square-planar and the coordination of the bridging oxygen is also planar. Within the planar four-membered copper-oxygen ring, the angle at copper is 76°; a molecular orbital treatment of the* π*-system suggests a relationship between this angle and the magnetic properties of binuclear copper(II) complexes.*

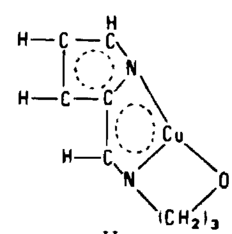
Introduction

As part of a general study of oxygen-bridged complexes, structures were reported[1] for the complexes of copper(II) and imines of acetylacetone and aminoalcohols; the structures and properties of these complexes were found to differ markedly with the size of the imino-alkoxide chelate ring. The complex, Ia, of the imine of 2-aminoethanol, was found to be tetrameric with a normal magnetic moment at room temperature; the imine of 3-amino-1-propanol (abbreviated PIA in formulas) gave a complex, Ib, which was dimeric with a subnormal magnetic moment at room temperature. From these observations and from a survey of other oxygen-bridged copper(II) complexes,[2-12] a general relationship between magnetic moments and the stereochemistry of the bridging oxygen was suggested - complexes with tetrahedral coordination about oxygen exhibit normal magnetic moments at room temperature and complexes with planar three-coordination about oxygen exhibit low magnetic moments. On the basis of these observations, an explanation of the spin coupling in $[Cu(PIA)]_2$, Ib, in terms of a delocalized π-system involving the $3d_{xz}$, $3d_{yz}$ orbital of the coppers and the $2p_z$ orbitals of the oxygens was suggested.[1]

In order to investigate further the effect of factors such as ring size and the extent of delocalization on structure and magnetic properties, we have prepared a complex, II, with a five-membered unsaturated ring and a six-membered saturated ring; in this paper we report the preparation, structure and properties of that complex.



Ia, n=2; Ib, n=3



II

Experimental Section

Preparation. Equimolar amounts (0.005 moles) of 3-amino-1-propanol and pyrrole-2-carboxaldehyde were mixed and dissolved in methanol. The above solution and a methanol solution containing 0.005 moles of potassium hydroxide were added simultaneously from dropping funnels to a warm stirred methanol solution of 0.005 moles of copper(II) acetate monohydrate. The resulting red-brown powder was allowed to air dry and then recrystallized from nitro-benzene; red needle-like crystals were obtained.

Anal. Calcd for $Cu(C_8H_{10}N_2O)$: C, 44.96; H, 4.72; N, 13.11. Found: C, 44.57; H, 5.05; N, 12.93.

Magnetic Susceptibility Measurement. The magnetic susceptibility of the compound was determined by

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(2) J.A. Bertrand, J.A. Kelley, and J.L. Breece, *Inorg. Chim. Acta, 4*, 247 (1970).
(3) H.L. Schafer, J.C. Morrow, and H.M. Smith, *J. Chem. Phys., 42*, 504 (1965).
(4) R.S. Sayer, R.J. Williams, and W.H. Watson, *Inorg. Chem.*, 6, 951 (1967).
(5) G.A. Barclay and B.F. Hoskins, *J. Chem. Soc.*, 1979 (1965).
(6) J.A. Bertrand and J.A. Kelley, *J. Am. Chem. Soc., 88*, 4746 (1966); J.A. Bertrand, *Inorg. Chem.*, 6, 495 (1967).
(7) B.T. Kilbourn and J.D. Dunitz, *Inorg. Chim. Acta, 1*, 209 (1967).
(8) J.A. Bertrand and J.A. Kelley, *Inorg. Chem., 8*, 1982 (1969).
(9) N.S. Gill and M. Sterns, *Inorg. Chem., 9*, 1619 (1970).
(10) J.A. Bertrand and J.A. Kelley, *Inorg. Chim. Acta, 4*, 526 (1970).
(11) J.A. Bevan, D.P. Graddon, and J.F. McConnell, *Nature, 199*, 373 (1963).
(12) A.T. Casey, B.F. Hoskins, and F.D. Williams, *Chem. Comm.*, 904 (1970).

the Faraday method at 26.5°C, using $HgCo(CNS)_4$ as a calibrant. Diamagnetic corrections were made using published atomc values.[13] For $Cu(C_8H_{10}N_2O)$: $\chi_g = 0.17\times10^{-6}$, $\chi_m^{corr} = 1200\times10^{-6}$, and $\mu_{eff} = 0.54$ B.M. per gram atom of copper(II).

Collection and Reduction of X-ray Data. A crystal of approximate dimensions $0.1 \times 0.1 \times 0.4$ mm was mounted along the long dimension (b-axis) on a glass fiber. Precession photographs were taken, using Zirconium-filtered Mo Kα radiation, $\lambda = 0.7106$ Å. The crystal was found to be monoclinic with a = 25.61(2) Å,[14] b = 5.46(1) Å, c = 16.90(2), and β = 136.33(10)° at 25°C. The density calculated on the basis of 8 formula units per unit cell, 1.74 g/cm^3, agrees well with the experimental value, 1.73(1) g/cm^3, obtained by the flotation method using a mixture of carbon tetrachloride and diiodomethane.

The absence of *hkl* reflections with $h+k = 2n+1$ and the absence of *k0l* reflections with $l = 2n+1$ indicated space group Cc (No. 9) or C2/c (No. 15). The space group ambiguity was resolved in favor of C2/c through the Patterson map and the successful refinement of the structure.

Intensity data were collected on the precession camera, using the same crystal as used for the space group determination. A total of 858 unique non-zero reflections were estimated visually from the *hkl* (l = 0-4) and the *hkl* (h = 0-6) layers. Lorentz-polarization corrections were computed but no corrections for absorption were made ($\mu = 27$ cm^{-1}).

Solution and Refinement of Structure. Computation were carried out on the Univac 1108 computer; programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy XFLS and ORFFE least squares, Johnson's ORTEP program for crystal structure illustrations, and various locally written programs.

The coordinates of the copper atoms were determined from a three-dimensional Patterson synthesis; after least-squares refinement of individual scale factors for each layer of data and the copper coordinates. a Fourier synthesis, phased on the copper atom, revealed the positions of all non-hydrogen atoms.

A Fourier synthesis phased on these atoms showed a definite anisotropic thermal motion of the copper atom; anisotropic thermal parameters were therefore assigned to the copper atom. At this point further structure-factor calculations and a difference Fourier phased on all the non-hydrogen atoms revealed the positions of all hydrogen atoms. All hydrogen atoms were introduced into the structure factor calculations with the isotropic temperature factor of the adjacent carbon; further full-matrix least-squares refinement (minimizing $\omega(|F_o|-|F_c|)^2$) of all parameters except hydrogen coordinates and hydrogen temperature factors converged to a conventional R_1 value ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.076 and a value of R_2 ($\{\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega(|F_o|)^2\}^{1/2}$) equal to 0.076 with all reflections weighted at unity. In the final cycle of refinement, there was no parameter shift greater than 1/10 of one esd. A final difference Fourier had no positive maxima greater than 0.5 e/Å^3.

In the structure factor calculations, the scattering factors tabulated by Ibers[15] were employed for all atoms.

The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I; the observed and calculated structure factors are given in Table II.

Table I. Final Positional and Thermal Parameters for $[Cu(C_8H_{10}N_2O)]_2$.

Atom	x	y	z	B, Å^2
Cu	0.2382(1)	0.0620(2)	0.0507(1)	2.2(1)[a]
O	0.3139(4)	0.194(1)	0.0641(6)	2.4(1)
N1	0.1665(5)	—0.063(2)	0.0489(8)	2.9(2)
N2	0.3005(5)	—0.209(1)	0.1564(8)	2.7(2)
C1	0.3901(6)	0.108(2)	0.1389(9)	2.6(2)
C2	0.4185(5)	—0.014(2)	0.2468(9)	2.7(2)
C3	0.3792(6)	—0.253(2)	0.2182(9)	2.6(2)
C4	0.2668(6)	—0.342(2)	0.172(1)	2.7(2)
C5	0.1924(6)	—0.266(2)	0.111(1)	2.6(2)
C6	0.1401(6)	—0.365(2)	0.105(1)	3.2(2)
C7	0.0765(7)	—0.207(2)	0.035(1)	4.2(3)
C8	0.0967(6)	—0.023(2)	0.003(1)	3.6(3)
H1C1	0.397	—0.010	0.104	
H2C1	0.431	0.240	0.175	
H1C2	0.464	—0.060	0.323	
H2C2	0.400	0.100	0.275	
H1C3	0.380	—0.365	0.175	
H2C3	0.402	—0.332	0.289	
HC4	0.290	—0.500	0.230	
HC6	0.140	—0.520	0.140	
HC7	0.024	—0.200	0.001	
HC8	0.055	0.100	—0.058	

[a] Anisotropic refinement of the thermal parameter of copper gave the expression: $\exp[-(16h^2+189k^2+47l^2+14hk+34hl+36kl)\times10^{-4}]$.

Discussion

The structure, Figure 1, consists of dimeric units; the coppers of the dimer are bridged by oxygens of the iminoalkoxide ligands. Interatomic distances and angles are given in Table III; selected least-squares planes are presented in Table IV. The copper is four coordinate and the copper and the four atoms bonded to copper are close to planar with none of the five more than 0.11 Å out of the best least-squares plane through O,N1,N2, and O'. The angles at copper are not the 90° angles expected for square-planar coordination but reflect the effect of ring size - the larger N–Cu–O angle (106.0(4)°) is not included in a ring, the other N–Cu–O angle (95.2(4)°) is in the six-membered chelate ring, the N–Cu–N angle (83.2(5)°) is in the five-membered chelate ring, and the O–Cu–O angle (76.1(4)°) is in the four-membered copper-oxygen ring. The four-membered copper-oxygen ring is exactly planar since there is an inversion center at the center of the ring; the coordination around the bridging oxygen is issentially planar with the carbon bonded to oxygen only 0.05 Å out of the plane of the

(13) B.N. Figgis and J. Lewis in « Modern Coordination Chemistry » J. Lewis and R.G. Wilkins, Ed., Intersciences Publishers, Inc., John Wiley and Sons, Inc., New York, N.Y., 1960, p. 403.
(14) Numbers in parentheses here and elsewhere in this paper indicate the estimated standard deviation in the least significant digits.

(15) J.A. Ibers in « International Tables for X-Ray Crystallography », Vol. 3, the Kynoch Press, Birminghan, England, 1962.

Table II. Observed and Calculated Structure Factors (in Electrons) for $[Cu(C_8H_{10}N_2O)]_2$.

H	K	FO	FC
L= 0			
4	0	565	446
6	0	1839	1924
8	0	901	844
10	0	300	352
12	0	839	825
14	0	743	667
16	0	513	478
18	0	323	306
3	1	378	348
5	1	851	871
7	1	780	758
9	1	750	717
11	1	867	857
13	1	1029	970
15	1	953	985
17	1	711	696
19	1	347	445
21	1	329	384
23	1	283	303
0	2	605	825
2	2	489	533
4	2	734	814
6	2	1374	1513
8	2	1130	1071
10	2	802	835
12	2	797	801
14	2	266	264
16	2	211	186
1	3	185	208
3	3	737	744
5	3	605	557
7	3	92	90
9	3	270	214
13	3	126	78
15	3	225	163
17	3	171	154
19	3	76	102
21	3	222	218
0	4	278	302
8	4	270	297
10	4	232	284
3	5	224	215
5	5	374	406
7	5	199	209
0	6	320	366
2	6	320	358
4	6	225	241
6	6	211	177
8	6	255	281
10	6	203	190
12	6	96	87
L= -1			
-17	1	158	129
-15	1	346	363
-13	1	396	428
-11	1	579	509
-9	1	867	768
-7	1	680	638
-5	1	607	587
-3	1	927	842
5	1	328	463
7	1	245	266
9	1	150	84
11	1	179	154
13	1	332	275
15	1	321	248
17	1	86	105
23	1	136	102
-22	2	291	259
-20	2	271	290

H	K	FO	FC
-18	2	283	265
-16	2	129	122
-14	2	150	156
-12	2	580	500
-10	2	408	447
-8	2	177	165
-6	2	118	119
-2	2	827	846
2	2	349	283
4	2	434	407
6	2	861	839
8	2	1006	1006
10	2	1020	992
12	2	908	836
14	2	832	583
16	2	368	368
18	2	340	324
20	2	377	398
22	2	253	248
-21	3	240	213
-19	3	285	264
-17	3	299	299
-15	3	391	440
-13	3	471	526
-11	3	342	415
-9	3	520	557
-7	3	1229	1273
-5	3	1632	1531
-3	3	888	898
-1	3	875	978
1	3	1273	1336
3	3	1236	1260
5	3	1005	986
7	3	727	706
9	3	685	635
11	3	306	287
15	3	153	144
17	3	183	165
19	3	94	107
21	3	95	116
-20	4	258	284
-18	4	394	393
-16	4	298	308
-14	4	324	330
-12	4	389	445
-10	4	311	313
-8	4	264	256
-6	4	211	207
-2	4	206	181
2	4	290	307
4	4	461	498
6	4	807	797
8	4	771	766
10	4	595	558
12	4	553	574
14	4	550	531
16	4	494	484
18	4	499	532
20	4	457	483
22	4	359	537
-17	5	151	143
-15	5	160	116
-13	5	162	171
-11	5	397	428
-9	5	589	639
-7	5	523	554
-5	5	450	519
-3	5	708	716
-1	5	562	625
1	5	386	411
3	5	562	596
5	5	708	731
7	5	551	590
9	5	370	423
11	5	283	224

H	K	FO	FC
-12	6	126	129
-10	6	159	197
-8	6	186	175
-6	6	132	134
-2	6	133	121
4	6	249	277
6	6	266	239
8	6	297	291
10	6	349	361
12	6	226	240
14	6	201	217
16	6	224	233
-3	7	201	186
-1	7	157	167
1	7	91	117
3	7	128	161
L= -2			
-20	0	321	333
-18	0	329	332
-16	0	294	356
-14	0	973	898
-12	0	1334	1344
-10	0	1040	967
-8	0	405	418
-6	0	878	860
-4	0	1421	1417
-2	0	1539	1506
6	0	489	550
8	0	679	790
10	0	636	666
12	0	125	118
14	0	139	139
18	0	235	201
20	0	325	305
22	0	344	325
24	0	319	295
26	0	228	195
-19	1	317	301
-17	1	264	291
-15	1	288	294
-13	1	269	234
-9	1	181	205
-7	1	73	93
-5	1	720	681
-3	1	312	354
-1	1	439	373
1	1	2234	2317
3	1	1307	1380
5	1	619	618
7	1	1658	1706
9	1	811	870
11	1	720	763
13	1	1688	1563
15	1	1228	1221
17	1	594	547
19	1	503	458
21	1	477	437
23	1	335	306
25	1	255	237
-20	2	196	181
-18	2	156	130
-16	2	304	336
-14	2	[illegible]	521
-12	2	386	413
-10	2	703	706
-8	2	1076	1112
-6	2	1008	959
-4	2	1155	1142
-2	2	1308	1418
2	2	817	845
6	2	258	258
8	2	931	919
10	2	236	179

H	K	FO	FC
12	2	118	102
14	2	89	112
16	2	286	299
18	2	452	436
20	2	150	139
22	2	157	146
24	2	196	180
26	2	158	165
-19	3	295	188
-17	3	158	163
-15	3	243	264
-13	3	181	187
-11	3	142	151
-9	3	192	180
-7	3	92	73
-5	3	89	118
1	3	618	587
3	3	832	727
5	3	421	397
7	3	816	744
9	3	887	823
11	3	450	416
13	3	331	354
15	3	315	311
17	3	232	187
19	5	264	231
21	3	157	150
-8	4	178	94
-6	4	142	113
-4	4	99	82
4	4	136	158
8	4	171	179
12	4	177	133
14	4	241	212
22	4	158	95
-17	5	151	160
-9	5	110	119
-7	5	327	274
-1	5	184	176
3	5	300	245
5	5	369	415
7	5	283	247
9	5	525	282
11	5	266	240
13	5	155	163
15	5	248	239
17	5	158	150
21	5	108	134
-14	6	148	163
-12	6	328	276
-10	6	248	227
-8	6	250	214
-6	6	388	417
-4	6	448	455
-2	8	336	312
0	6	274	280
2	6	296	269
4	6	158	168
10	6	224	190
12	6	112	130
-3	7	156	126
-1	7	272	275
1	7	315	295
3	7	295	277
5	7	315	271
7	7	247	222
9	7	290	251
11	7	304	310
13	7	233	249
15	7	196	209
L= -3			
-17	1	164	210
-15	1	330	363

H	K	FO	FC
-13	1	291	322
-11	1	270	283
-9	1	351	380
-7	1	226	260
-5	1	226	254
-3	1	247	310
-1	1	302	251
9	1	165	194
11	1	872	796
13	1	736	666
15	1	85	165
17	1	132	132
19	1	100	130
21	1	153	135
23	1	229	178
25	1	120	170
27	1	246	258
-10	2	169	121
-8	2	204	184
-6	2	400	484
-4	2	708	864
-2	2	1030	1074
2	2	832	969
4	2	726	841
6	2	770	798
8	2	1310	1355
10	2	1198	1275
12	2	793	760
14	2	852	797
16	2	911	912
18	2	647	626
20	2	307	303
22	2	162	169
-19	3	300	316
-17	3	363	380
-15	3	234	233
-13	3	338	350
-11	3	612	717
-9	3	925	854
-7	3	939	904
-5	3	1123	1056
-3	3	912	826
-1	3	352	332
1	3	227	154
3	3	398	441
5	5	513	450
11	3	246	219
13	5	138	123
15	3	354	371
17	3	399	394
19	3	417	481
21	3	464	473
23	3	360	380
25	3	273	270
27	3	171	160
-10	4	196	145
-8	4	351	313
-6	4	457	530
-4	4	447	487
-2	4	413	372
2	4	846	745
4	4	1011	1031
6	4	1364	1429
8	4	1128	1160
10	4	876	788
12	4	524	556
14	4	290	263
16	4	318	283
18	4	401	376
20	4	291	282
22	4	271	262
24	4	211	195
-17	5	204	222
-15	5	296	296
-13	5	271	300

H	K	FO	FC
-11	5	340	341
-9	5	411	383
-7	5	438	383
-5	5	433	414
-3	5	362	356
-1	5	321	256
1	5	357	354
3	5	338	314
5	5	159	124
7	5	113	72
9	5	114	112
11	5	346	341
13	5	309	294
15	5	118	129
17	5	189	124
19	5	209	219
21	5	242	251
23	5	168	175
-6	6	210	162
-4	6	271	276
-2	6	363	382
2	6	209	172
4	6	362	355
6	6	295	282
8	6	120	125
10	6	320	275
12	6	364	382
14	6	272	289
16	6	243	226
18	6	208	194
20	6	117	95
L= -4			
-16	0	314	399
-14	0	439	383
-12	0	999	1026
-10	0	838	916
-8	0	902	903
-6	0	1058	1113
-4	0	726	680
-2	0	647	746
10	0	1026	1079
12	0	551	525
14	0	1163	1124
16	0	1135	1126
18	0	887	910
20	0	838	809
22	0	523	562
24	0	409	439
26	0	434	478
-13	1	304	366
-11	1	357	425
-9	1	368	368
-7	1	711	687
-5	1	902	974
-3	1	919	950
-1	1	1522	1457
9	1	1585	1684
11	1	1612	1437
13	1	991	1014
15	1	912	892
17	1	405	430
21	1	187	180
23	1	141	169
-16	2	286	320
-14	2	356	428
-12	2	365	456
-10	2	128	147
-8	2	85	103
-6	2	612	554
-4	2	798	751
-2	2	693	626
2	2	680	602
4	2	324	241

H	K	FO	FC
6	2	167	132
8	2	526	495
10	2	565	463
12	2	198	180
14	2	728	682
16	2	828	786
18	2	280	259
20	2	284	298
22	2	376	424
24	2	237	238
26	2	192	209
-7	3	241	228
-5	3	123	101
-3	3	342	337
-1	3	561	472
1	3	152	113
3	3	234	211
5	3	295	349
7	3	398	363
9	3	719	621
11	3	305	349
13	3	256	187
15	3	380	374
17	3	133	157
19	3	98	51
21	3	252	167
23	3	107	68
-8	4	288	230
-6	4	297	265
-4	4	215	225
2	4	223	175
4	4	271	267
6	4	272	278
8	4	275	229
10	4	93	63
12	4	165	154
14	4	98	73
-9	5	110	132
-7	5	216	168
-5	5	320	283
-3	5	315	265
-1	5	180	148
1	5	178	194
3	5	290	273
7	5	103	117
9	5	254	265
11	5	256	240
13	5	183	205
15	5	152	163
17	5	109	102
19	5	111	105
-10	6	160	186
-6	6	160	184
-4	6	194	196
-2	6	193	216
6	6	111	82
14	6	159	107
16	6	160	169
18	6	226	229
20	6	159	159
22	6	111	118
-11	7	105	153
-9	7	155	126
-1	7	198	242
1	7	324	336
3	7	257	269
5	7	325	272
7	7	324	324
9	7	256	242
11	7	228	219
13	7	197	219
15	7	112	138
17	7	111	119

K	L	FO	FC
H= 0			
0	2	2061	2035
0	4	484	408
0	6	519	526
0	8	856	853
0	10	962	1036
0	12	347	398
0	14	136	110
2	1	873	926
2	2	981	1050
2	3	1265	1208
2	4	884	873
2	5	653	652
2	6	279	265
2	7	393	396
2	8	291	293
2	10	526	513
2	11	153	177
2	12	235	196
2	13	248	246
2	14	108	110
4	1	158	169
4	3	639	594
4	4	270	383
4	5	653	553
4	7	581	529
4	8	131	132
4	9	243	237
4	11	108	90
6	3	228	238
6	5	318	367
8	6	148	144
6	7	161	186
8	8	154	194
H= 1			
1	-14	327	367
1	-12	492	534
1	-11	211	235
1	-9	329	407
1	-8	564	558
1	-7	570	561
1	-6	1898	1784
1	-5	116	92
1	-4	2392	2499
1	-3	2086	2214
1	-1	117	97
1	0	117	164
1	2	375	373
1	3	291	251
1	4	1644	1457
1	5	445	377
1	6	1176	1123
1	7	608	478
1	8	978	863
1	9	517	500
1	11	335	284
1	12	393	340
1	14	422	359
3	-13	187	195
3	-11	447	470
3	-9	474	475
3	-8	118	112
3	-7	365	408
3	-6	355	416
3	-5	189	191
3	1	933	976
3	3	339	332
3	4	464	472
3	5	158	125
3	6	262	223
3	7	336	269
3	8	122	159

K	L	FO	FC
3	9	503	438
3	11	455	437
5	-11	127	186
5	-9	391	421
5	-7	183	184
5	-5	128	41
5	1	584	625
5	2	189	176
5	3	286	256
5	4	128	148
5	6	225	233
5	7	225	256
5	9	366	368
5	11	121	184
7	1	123	167
7	2	212	275
7	4	204	242
H= 2			
0	-12	707	746
0	-10	1093	1144
0	-8	1498	1465
0	-6	643	715
0	-4	1779	1679
0	2	1749	1586
0	4	687	746
0	6	221	206
0	8	958	974
0	10	703	658
0	12	197	153
0	14	250	183
2	-15	321	340
2	-13	277	255
2	-12	232	250
2	-11	129	116
2	-10	326	413
2	-9	166	182
2	-8	798	761
2	-7	587	578
2	-6	856	775
2	-5	927	914
2	-2	788	845
2	1	754	846
2	2	1320	1418
2	3	923	1074
2	4	602	626
2	5	1013	1062
2	6	158	161
2	7	643	610
2	8	476	429
2	10	597	456
2	11	239	214
2	12	549	487
2	13	143	126
4	-13	245	257
4	-11	197	210
4	-8	133	136
4	-7	261	258
4	-5	698	681
4	1	177	181
4	3	402	372
4	5	653	611
4	7	604	579
4	8	168	192
4	9	279	237
4	13	133	171
6	-8	139	192
6	-7	198	266
6	-6	199	239
6	-5	346	393
6	-2	245	269
6	1	141	121
6	2	283	312

K	L	FO	FC
6	3	316	382
6	4	199	216
6	5	372	365
6	6	139	119
H= 3			
1	-16	168	226
1	-14	450	464
1	-13	108	140
1	-12	436	476
1	-11	275	278
1	-10	343	355
1	-9	321	352
1	-8	196	125
1	-7	1284	1223
1	-6	1455	1385
1	-5	472	479
1	-4	2491	2561
1	-3	2430	2473
1	1	803	842
1	2	411	354
1	3	334	310
1	4	927	950
1	5	158	115
1	6	1008	1000
1	7	340	297
1	8	611	574
1	10	107	110
1	11	354	297
1	14	169	218
3	-13	162	187
3	-11	306	321
3	-9	538	543
3	-8	311	280
3	-7	406	446
3	-6	263	266
3	-5	364	371
3	1	891	898
3	3	831	826
3	4	325	337
3	6	429	446
3	7	404	346
3	8	373	346
3	9	544	504
3	11	286	244
5	-11	286	295
5	-9	432	405
5	-7	322	325
5	-6	226	194
5	1	791	716
5	3	391	356
5	4	321	285
5	5	280	247
5	6	283	248
5	7	232	192
5	9	286	287
5	11	226	237
7	-6	229	202
7	1	164	186
7	6	187	257
H= 4			
0	-16	252	292
0	-12	341	402
0	-10	1258	1308
0	-8	1244	127
0	2	1309	1417
0	4	719	680
0	6	90	110
0	8	979	926
0	10	432	417
0	12	177	197

K	L	FO	FC
0	14	260	237
2	-15	306	329
2	-13	326	302
2	-12	222	202
2	-11	368	377
2	-10	378	325
2	-9	136	123
2	-8	1191	1247
2	-7	1193	1243
2	-6	1293	1276
2	-5	1336	1278
2	2	1086	1142
2	3	717	674
2	4	809	751
2	5	1000	878
2	6	141	152
2	7	526	487
2	8	191	143
2	10	418	340
2	12	478	435
4	-13	308	299
4	-12	123	159
4	-11	171	208
4	-10	119	76
4	-8	229	187
4	-7	318	300
4	-5	982	965
4	3	502	487
4	4	228	225
4	5	736	776
4	7	593	528
4	9	251	227
6	-10	180	146
6	-9	128	121
6	-8	181	208
6	-7	256	271
6	-6	313	266
6	-5	404	397
6	2	478	455
6	3	286	276
6	4	181	196
6	5	181	209
H= 5			
1	-14	464	511
1	-13	190	221
1	-12	464	529
1	-11	137	146
1	-10	446	499
1	-9	377	436
1	-8	154	147
1	-7	1099	1038
1	-6	420	404
1	-5	403	426
1	1	620	587
1	2	739	681
1	3	303	254
1	4	1049	974
1	5	439	411
1	6	961	916
1	8	307	390
1	10	380	328
1	11	251	241
3	-12	234	249
3	-11	507	569
3	-10	438	469
3	-9	821	839
3	-7	595	667
3	-5	496	527
3	1	1514	1531
3	2	98	118
3	3	1018	1056
3	4	105	101

K	L	FO	FC
3	5	153	150
3	6	503	503
3	7	451	375
3	8	340	297
3	9	512	470
3	11	262	248
5	-11	317	279
5	-10	181	227
5	-9	506	536
5	-7	527	585
5	-6	246	223
5	-5	122	83
5	-4	172	114
5	1	523	519
5	3	500	414
5	4	309	283
5	5	296	227
5	9	264	261
5	11	183	257
H= 6			
0	-16	260	241
0	-14	165	155
0	-12	205	164
0	-10	1214	1378
0	-8	547	535
0	2	709	860
0	4	1017	1113
0	6	403	321
0	8	281	248
0	10	314	274
0	12	276	219
2	-16	190	240
2	-15	182	177
2	-13	409	373
2	-12	112	112
2	-11	585	643
2	-10	202	211
2	-8	846	858
2	-7	1046	1037
2	-6	894	830
2	-5	806	702
2	1	140	119
2	2	958	959
2	3	513	464
2	4	545	554
2	5	459	415
2	7	521	445
2	8	172	122
2	9	313	245
2	10	420	376
4	-15	197	239
4	-13	536	514
4	-11	362	343
4	-8	417	592
4	-7	473	373
4	-5	1151	1105
4	1	252	207
4	2	119	113
4	3	546	530
4	4	249	265
4	5	698	726
4	7	596	539
4	9	278	262
6	-10	200	194
6	-8	244	255
6	-7	198	220
6	-6	280	247
6	-5	279	263
6	2	526	417
6	3	199	162
6	5	142	171

four-membered ring. The five-membered delocalized chelate ring is essentially planar with no atom of the ring more than 0.02 Å out of the best least-squares plane through the ring; the five-membered pyrrole ring is planar to within 0.01 Å.

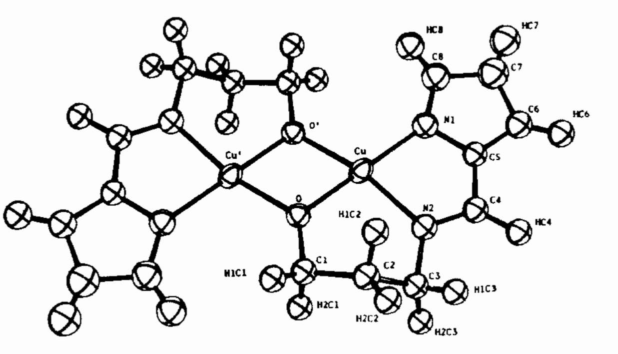

Figure 1. ORTEP plot of the molecular structure of $Cu(C_8H_{10}N_2O)$. The thermal ellipsoids and spheres are at the 50% probability level.

As in other polynuclear structures in which the coordination of the bridging oxygen is planar, the room temperature magnetic moment (0.54 B.M.) is considerably below the value expected for one unpaired electron per copper. An explanation of the spin-coupling in such systems in terms of a delocalized π-system involving the $3d_{xz}$, $3d_{yz}$ orbitals of the coppers and the $2p_z$ orbitals of the oxygens has been suggested. A molecular orbital treatment of these six orbitals indicates two anti-bonding orbitals of different symmetries; since these orbitals can, thus, have different energies, it is possible for the dimer to have a singlet ground state and a thermally accessible triplet state.

Although the energy difference between the anti-bonding π-orbitals of the present compound could result from interactions with the chelate π-system, the reason for an energy difference between the corresponding π-orbitals of complexes such as $[Cu(PyO)Cl_2]_2$ (where PyO represents pyridine-N-oxide), which also exhibit sub-normal magnetic moments at room temperature,[16] was not apparent from the previous treatment. Furthermore, planar four-membered rings are also present in chloride-bridged complexes of copper(II) and the room temperature moments of those compounds are normal. A review of the available structure data on oxygen-bridged[1-12] and chloride-bridged[17-22] complexes of copper(II) reveals an important difference: in all of the oxygen-bridged complexes with sub-normal room temperature magnetic moments the O–Cu–O angles within the four-membered ring are considerably less than 90° (usually near 70°); in the chloride-bridged complexes, the Cl–Cu–Cl

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(17) P.H. Vossos, L.D. Jennings, and R.E. Rundle, *J. Chem. Phys.*, *32*, 1590 (1960).
(18) P.H. Vossos, D.R. Fitwater, and R.E. Rundle, *Acta. Cryst.*, *15*, 1037 (1963).
(19) R.D. Willet, C. Dwiggins, Jr., R.F. Kruh, and R.E. Rundle, *J. Chem. Phys.*, *38*, 2429 (1963).
(20) R.D. Willett and R.E. Rundle, *J. Chem. Phys.*, *40*, 838 (1964).
(21) R.S. Sager and W.H. Watson, *Inorg. Chem.*, *7*, 2034 (1968).
(22) D.J. Hodgson, P.K. Hale, J.A. Barnes, and W.E. Hatfield, *Chem. Comm.*, 786 (1970).

Table III. Interatomic Distances and Angles for $[Cu(C_8H_{10}N_2O)]_2$.

Atoms	Distance, Å	Atoms	Angle, degrees
Cu-Cu'	3.001((4)	Cu-N1-C5	110.7(9)
Cu-O	1.920(11)	C5-N1-C8	106.9(12)
Cu-O'	1.891(7)	Cu-N1-C8	142.2(9)
Cu-N1	1.942(13)	N1-C8-C7	111.1(11)
Cu-N2	1.952(9)	C6-C7-C8	103.7(14)
O-C1	1.435(13)	C5-C6-C7	107.0(12)
N1-C5	1.328(14)	N1-C5-C6	111.3(11)
N1-C8	1.353(18)	N1-C5-C4	117.4(13)
N2-C3	1.472(16)	C4-C5-C6	131.3(11)
N2-C4	1.293(20)	N2-C4-C5	115.4(10)
C1-C2	1.543(20)	Cu-N2-C4	113.0(8)
C2-C3	1.499(15)	Cu-N2-C3	124.5(9)
C4-C5	1.420(17)	C3-N2-C4	122.4(9)
C5-C6	1.379(24)	N2-C3-C2	109.9(9)
C6-C7	1.414(16)	C1-C2-C3	111.3(9)
C7-C8	1.410(23)	O-C1-C2	111.2(13)
C1-H1C1	0.97	Cu-O-C1	126.4(7)
C1-H2C1	1.03	Cu-O-Cu'	103.9(4)
C2-H1C2	0.95	C1-O-Cu'	129.6(9)
C2-H2C2	1.08	O-Cu-N2	95.2(4)
C3-H1C3	0.96	N1-Cu-N2	83.2(5)
C3-H2C3	0.97	N1-Cu-O'	106.0(4)
C4-HC4	1.10	O-Cu-O'	76.1(4)
C6-HC6	1.03	O-C1-H1C1	114
C7-HC7	1.01	H1C1-C1-H2C1	106
C8-HC8	1.03	C2-C1-H2C1	101
		C1-C2-H1C2	141
		H1C2-C2-H2C2	93
		C3-C2-H2C2	104
		C2-C3-H1C3	115
		H1C3-C3-H2C3	109
		N2-C3-H2C3	104
		N2-C4-HC4	128
		C5-C4-HC4	117
		C5-C6-HC6	133
		C7-C6-HC6	120
		C6-C7-HC7	139
		C8-C7-HC7	117
		C7-C8-HC8	117
		N1-C8-HC8	132

Table IV. Equations [a] of Least-Squares Atomic Planes and Distances of Atoms(Å) from these Planes for $[Cu(C_8H_{10}N_2O)]_2$

(a) Equation of the Plane Including (Cu,O,Cu'):

$$0.216X-0.435Y-0.874Z=0.791$$

Atoms	Distance from Plane Å	Atom	Distance from Plane Å
Cu	0.000	C4	0.201
O	0.000	C5	0.070
N1	—0.086	C6	0.063
N2	0.191	C7	—0.134
C1	0.053	C8	—0.215
C2	—0.302	Cu'	0.000
C3	0.275	O'	0.000

(b) Equation of the Least-Squares Plane [b] of the Coordination Sphere (O,N1,N2,O'):

$$0.205X-0.410Y-0.888Z=0.749$$

Atoms		Atom	
Cu	—0.032	C4	—0.069
O	—0.039	C5	—0.012
N1	—0.114	C6	0.016
N2	0.072	C7	—0.153
C1	—0.042	C8	—0.205
C2	—0.454	Cu'	0.043
C3	—0.109	O'	0.051

[a] Direction cosines of the plane refer to the orthogonal axis system a,b,c*. [b] All atoms weighted at unity.

angles approach 90°. By incorporating these observations into the treatment of the pπ–dπ system, it is possible to give an explanation of the energy difference between the anti-bonding orbitals in all of the oxygen-bridged copper(II) complexes that show subnormal room temperature magnetic moments. The treatment employed has been presented previously[23-25] in a general treatment of pπ–dπ systems but has not been applied to transition metal complexes.

Although the actual symmetry of the complexes is usually lower, the four-membered ring in several of the low-moment compounds approaches D_{2h} symmetry. Using the coordinate system previously suggested[3], the six π-orbitals, Figure 2, transform in D_{2h} symmetry as $A_u+B_{2g}+2B_{1u}+2B_{3g}$; suitable combinations of atomic orbitals which transform with these symmetries are indicated in Figure 3. Of these, the A_u and B_{2g} combinations are non-bonding and there are bonding and anti-bonding combinations with both B_{1u} and B_{3g} symmetries.

Considerations of the B_{1u} and B_{3g} combinations indicates that the two would have identical overlap of copper and oxygen orbitals for an O–Cu–O angle of 90°; however, as the O–Cu–O angle is decreased, the

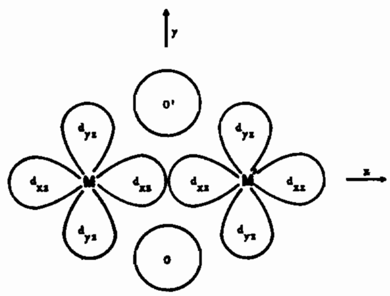

Figure 2. Projection of the six π-orbitals onto the xy plane.

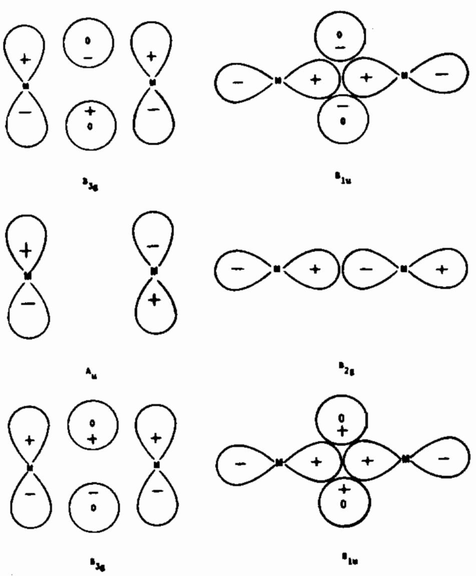

Figure 3. Symmetry adapted linear combinations of atomic orbitals.

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(24) D.P. Craig, Special Publication No. 12, The Chemical Society, London, 1958, p. 343.
(25) D.P. Craig and K.A.R. Mitchell, *J. Chem. Soc.*, 4682 (1965).

overlap of the B_{1u} combination is increased and that of the B_{3g} combination is decreased. For an O–Cu–O angle of 90°, the B_{1u} and B_{3g} anti-bonding orbitals would, therefore, have the same energy unless they were affected by other factors such as different interactions with a chelate π-system.

In addition to the dependence on the angle at copper, the energy separation would depend on the energies of the oxygen orbitals and the copper orbitals and, since these energies depend on the bonding to the rest of the molecule, the nature of the rest of the molecule would affect the magnitude of the energy difference. This factor is reflected in the variation of J, the coupling constant, with the electron density at oxygen as observed[26] for a series of complexes with substituted pyridine oxides as bridging groups; it also accounts for the difference in magnetic moments observed for compounds such as $[Cu(PIA)]_2$[1] and $[Cu(PyO)Cl_2]_2$[4], both of which have O-Cu-O angles of approximately 72°.

The above treatment appears to qualitatively explain the observed magnetic moments of oxygen-bridged copper(II) complexes; it is also possible to show that such a treatment gives singlet-triplet separations of the right magnitude. Experimental values are available - the temperature dependence of the magnetic susceptibilites of a number of oxygen-bridged copper(II) dimers have been studied[26-28] and have been found to fit the equation[29]:

$$\chi_M = (2g^2\beta^2N/3kT)[1+1/3\exp(J/kT)]^{-1} + N\alpha$$

where χ_M is the molar susceptibility of the dimer, g is the Lande factor, β is the Bohr magneton, N, is Avogadro's number, k is the Boltzmann constant, $N\alpha$ is the temperature independent paramagnetism, and J is the singlet-triplet energy separation. Values for J have usually been less than 500 cm^{-1}; from the room temperature susceptibility of $[Cu(C_8H_{10}N_2O)]_2$ (0.54 B.M.) a J value of ca. 560 cm^{-1} is obtained.

For purposes of energy calculations, it is convenient to write B_{1u} orbitals in terms of separate oxygen and copper orbitals:

$$\varphi_1(B_{1u}) = (p_z + p_z')/\sqrt{2}$$

$$\varphi_2(B_{1u}) = (d_{xz} + d_{xz}')/\sqrt{2}$$

In terms of the general treatment[23,24], these correspond to φ_0^A and φ_0^B. Using a Huckel approximation with the following definitions,

$$H_{11} = \int \varphi_1 H \varphi_1 d\tau = \alpha$$

$$H_{22} = \int \varphi_2 H \varphi_2 d\tau = \int d_{xz} H d_{xz} d\tau = \alpha_{xz}$$

$$H_{21} = H_{12} = \int \varphi_1 H \varphi_2 d\tau = 1/2 \int (p_z + p_z') H (d_{xz} + d_{xz}') d\tau = 2\int p_z H d_{xz} d\tau = 2\beta_{xz},$$

the secular equation is:

$$\begin{vmatrix} \alpha - E & 2\beta_{xz} \\ 2\beta_{xz} & \alpha_{xz} - E \end{vmatrix} = 0$$

and

$$E = \tfrac{1}{2}(\alpha + \alpha_{xz} \pm [(\alpha - \alpha_{xz})^2 + 16\beta_{xz}^2]^{1/2}.$$

For the B_{3g} orbitals, the appropriate linear combinations of oxygen and copper orbitals are:

$$\varphi_1(B_{3g}) = (p_z - p_z')/\sqrt{2}$$

$$\varphi_2(B_{3g}) = i(d_{yz} - d_{yz}')/\sqrt{2}$$

In terms of the general treatment[23,24], these correspond to φ_1^A and φ_1^B. Using the same definitions as before, the secular equation may be writen

$$\begin{vmatrix} \alpha - E & -2i\beta_{yz} \\ 2i\beta_{yz} & \alpha_{yz} - E \end{vmatrix} = 0$$

and

$$E = \tfrac{1}{2}(\alpha + \alpha_{yz} \pm [(\alpha - \alpha_{yz})^2 + 16\beta_{yz}^2]^{1/2}).$$

Although α_{xz} and α_{yz} may differ due to interactions with the rest of the molecule, the difference in most compounds is probably not very large and we have used $\alpha_{xz} = \alpha_{yz} = \alpha_d$; however, for an O–Cu–O angle other than 90°, different values are necessary for β_{xz} and β_{yz}. The energy difference, J, for the two antibonding orbitals is given by:

$$J = \tfrac{1}{2}([(\alpha - \alpha_d)^2 + 16\beta_{yz}^2]^{1/2} - [(\alpha - \alpha_d)^2 + 16\beta_{xz}^2]^{1/2}).$$

Although there is considerable question about the numerical values to be used, we have used valence state ionization energies[30] for the α's; for the β values, we have used

$$\beta = S_{ij}(\alpha + \alpha_d)\cos\gamma$$

where γ is the angle between Cu–O direction and the plane of the d orbital; the cos γ term was included[23,24] to account for the angular dependence of the overlap. The overlap integral was obtained from tabulated values[31] in the literature. With these values we calculate a J value of $[Cu(C_8H_{10}H_2O)]_2$ (*ca.* 870 cm^{-1}) which is of the same magnitude as the observed values.

It thus appears that the low room temperature magnetic moments of oxygen-bridged copper(II) complexes can be explained in terms of a delocalized π-system; it is probable that the same explanation applies to complexes of other metal ions. The same explanation can also be used to explain the low moment observed for CuF_2 since the F-Cu-F angle is 76°.

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