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Polynuclear Copper(II) Complexes with Oxygen Bridges: The Relationship between Magnetic Properties and Structure

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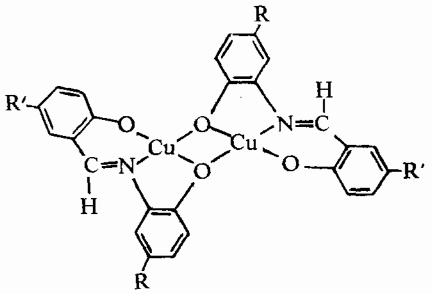
The structures of two copper(II) complexes of the general formula CuL (where L represents the dianion of $H_3C-C(O)-CH_2-C(CH_3)=N-(CH_2)_n-OH$) have been determined by single-crystal X-ray diffraction studies. The compound with $n=2$, abbreviated Cu(EIA), crystallizes as tetragonal crystals ($a=b=14.46$ Å, $c=7.63$ Å) of space group $P\bar{4}2_1c$ with two tetramers per unit cell ($\rho_{obsd}=1.70$; $\rho_{calcd}=1.71$ g/cm^3); the compound with $n=3$, abbreviated Cu(PIA), crystallizes as monoclinic crystals ($a=5.98$ Å, $b=10.97$ Å, $c=14.42$ Å, and $\beta=106.75°$) of space group $P2_1/c$, with two dimers per unit cell ($\rho_{obsd}=1.61$; $\rho_{calcd}=1.61$ g/cm^3). Both structures were solved from Patterson and electron density maps and refined by least-squares methods to conventional R values of 8.9% and 10.0% for Cu(EIA) and Cu(PIA), respectively. The two structures differ in the coordination about the bridging oxygens — in Cu(EIA) the oxygen is tetrahedrally coordinated and in Cu(PIA) the three — coordinate oxygen is planar. The fourth outer orbital of the planar oxygen and the d_{xz}, d_{yz} orbitals of copper can overlap to form a delocalized π-system; the pairing of electrons in delocalized π-orbitals is suggested as an explanation of the singlet ground state observed for most oxygen-bridged copper(II) complexes.

Introduction

A large number of copper(II) complexes are known to exhibit room temperature magnetic moments considerably below the spin-only value for one unpaired electron;[2] the temperature dependence of the magnetic susceptibilities of these compounds can be explained on the basis of a singlet ground state and a thermally accessible triplet state. Although they have similar magnetic properties, structure studies have indicated[3-5] that there are at least two different types of compounds - those with direct metal-metal bonding and those with oxygen bridges.

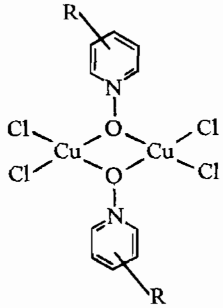
The copper(II) acetate dimer[3] is an example of the first type; there has been considerable discussion of the type of interaction involved. Both a σ-interaction, involving, d_{z^2} orbitals, and a Δ-interaction, involving $d_{x^2-y^2}$ orbitals, have been suggested.

In the second type of compound, of which $CuCl_2$-(Pyridine oxide)[5] is an example, the distance between copper ions (3.23 Å) is large enough to rule out direct interaction between copper orbitals and an interaction through the bridging oxygens has been assumed. A σ-type interaction, involving the copper(II) $d_{x^2-y^2}$ orbitals, has been used to explain the properties of a number of complexes[6] of the type:



All of these compounds were assumed to have the structure found[4] for the compound with R=H and R'=H.

The possibility of a π-type interaction between d_{xz} and d_{yz} orbitals of the copper ions and the oxygen p_z orbitals has also been suggested[7,8] and correlated with substituent effects in compounds of the type:



There are also examples of compounds with similar formulas which show different magnetic proper-

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(1) Alfred P. Sloan Research Fellow, 1966-1968.
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ties.[9-11] A series of compounds of the general formula $Cu(R_2NCH_2CH_2O)X$ has been studied;[9] some of the compounds have normal moments at room temperature, other have sub-normal moments, and at least one crystallizes in two different forms- one with a normal and one with a sub-normal moment.

The copper(II) compound[10] of the Schiff base of 2-aminoethanol and acetylacetone (hereafter referred to as Cu(EIA)) has a normal magnetic moment at room temperature while the Schiff base complex of o-aminophenol and acetylacetone has a sub-normal moment. Although structural data are available for the latter compound,[4] the presence of two different types of copper(II) ions (4- and 5-coordinate) and two different types of bridging oxygens (μ_2 and μ_3) makes it difficult to relate the magnetic properties to structural features.

To obtain additional information about magnetic interactions in these compounds, an investigation of structures of oxygen-bridged complexes with normal moments and similar complexes with sub-normal moments was initiated. On the assumption that the normal moment of the Schiff base complex of 2-aminoethanol, Cu(EIA), is in some way related to steric factors in the bonding of the ligand to the metal, the corresponding complex of 3-amino-1-propanol (hereafter abbreviated Cu(PIA)) was prepared. In this paper we report the preparation, magnetic moment and structure of Cu(PIA) and the structure of Cu(EIA). A preliminary report of the structure of Cu(EIA) has been published.[12]

Experimental Section

Preparations. Equimolar amounts of 2,4-pentanedione, the appropriate aminoalcohol, and potassium hydroxide were mixed, the mixture was dissolved in methanol, and a methanol solution containing an equivalent amount of copper(II) acetate was added; the crystalline product was filtered and then dried in vacuum.

Anal. Calcd. for Cu(PIA), $CuC_8H_{13}NO_2$: Cu, 29.05; C, 43.92; H, 6.00; N, 6.40. Found: Cu, 28.62; C, 44.07; H, 5.96; N, 6.30. Calcd. for Cu(EIA), $CuC_7H_{11}NO_2$: Cu, 31.04; C, 41.06; H, 5.43; N, 6.84. Found: Cu, 30.85; C, 41.12; H, 5.37; N, 6.78.

Magnetic Susceptibilities. The magnetic susceptibilities of the compounds were determined by the Gouy method at 25°C., using $HgCo(CNS)_4$ as a calibrant. Diamagnetic corrections were made using published atomic values.[13] For Cu(PIA): $\chi_G = -0.15$, $\chi_M^{corr} = 69$, and $\mu_{eff} = 0.41$ B.M.; for Cu(EIA): $\chi_G = 6.71$, $\chi_M^{corr} = 1463$, and $\mu_{eff} = 1.87$ B.M. The value reported for Cu(EIA) agrees with that previously reported.[10]

Collection and Reduction of X-ray Data

Cu(PIA). A needle-like crystal with approximate dimensions $0.10 \times 0.17 \times 0.60$ mm was mounted along the long dimension and precession photographs were taken, using zirconium-filtered Mo Kα radiation, $\lambda = 0.7106$ Å. The crystal was found to be monoclinic with $a = 5.98(1)$Å,[14] $b = 10.97(2)$ Å, $c = 14.42(2)$ Å, and $\beta = 106.75(10)$°. The density calculated on the basis of 4 formula units per unit cell, 1.61 g/cm^3, agrees well with the experimental value, 1.61(2) g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and diiodomethane.

The systematic absence of the reflections with $l = 2n+1$ on the $h0l$ zone and the systematic absence of the reflections with $k = 2n+1$ on the $0k0$ line were consistent only with space group $P2_1/c$ (No. 14).

Intensity data were collected on the precession camera, using the same crystal as used for the space group determination; a total of 631 unique, non-zero reflections were estimated visually from the hkl (l = 0-3) and hkl (k = 0-2) layers. Lorentz-polarization corrections were computed but no corrections for absorption were made ($\mu = 24$ cm^{-1}).

Cu(EIA). A needle-like crystal with approximate dimensions $0.10 \times 0.15 \times 0.60$ mm was mounted along the long dimension and precession photographs were taken using zirconium-filtered molybdenum Kα radiation ($\lambda = 0.7106$ Å). The crystal was found to be tetragonal with $a = b = 14.46(2)$ Å and $c = 7.63(2)$ Å. The density calculated on the basis of 8 formula units per unit cell, 1.71 g/cm^3, agrees well with the experimental value of 1.70(2) g/cm^3 obtained by the flotation method in a mixture of carbon tetrachloride and diiodomethane.

The systematic absence of the hhl reflections with $l = 2n+1$ and the systematic absence of $h00$ reflections with $h = 2n+1$ were consistent with space group $P\bar{4}2_1c$ (No. 114).

Intensity data were collected with the precession camera, using the same crystal used for the space group determination; a total of 394 unique, non-zero reflections were estimated visually for the hkl (k = 0-4) and the hhl layers. Lorentz-polarization corrections were computed but no corrections for absorption were made ($\mu = 31$ cm^{-1}).

Table I. Final Positional and Thermal Parameters for Cu(PIA).

Atom	x	y	z	B, A^2
Cu1	0.1068(4)	0.0322(2)	0.1055(2)	4.02(6)
O2	−0.1465(21)	0.0659(13)	−0.0015(9)	4.89(30)
C3	−0.3369(33)	0.1486(21)	−0.0102(15)	5.04(44)
C4	−0.1792(38)	0.2189(26)	0.1710(18)	6.20(52)
N5	0.0297(25)	0.1377(17)	0.2013(12)	4.57(34)
C6	0.1506(34)	0.1398(22)	0.2908(16)	4.96(44)
C7	0.0719(37)	0.2174(25)	0.3636(17)	6.31(54)
C8	0.3489(31)	0.0695(20)	0.3327(14)	4.66(41)
C9	0.4662(34)	−0.0068(24)	0.2819(15)	5.67(47)
C10	0.6916(35)	−0.0719(22)	0.3353(16)	5.79(49)
O11	0.3762(22)	−0.0275(15)	0.1892(10)	5.59(31)
C12	−0.2506(40)	0.2544(25)	0.0637(20)	8.07(65)

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[9] E. Uhlig and K. Staiger, *Z. anorg. allg. Chem.*, *346*, 21 (1966).

[10] E. G. Jager, *Z. Chem.*, *6*, 111 (1966).

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[14] Numbers in parentheses here and elsewhere in this paper indicate the estimhated standard deviation in the least significant digits.

Table II. Observed and Calculated Structure Factors (Electrons × 10) for Cu(PIA)

L=0			
H	K	FO	FC
0	4	693	683
0	6	210	150
0	0	224	198
0	2	133	114
1	3	587	535
1	4	197	176
1	5	216	191
1	6	56	67
1	7	252	250
1	9	152	133
1	0	118	115
1	1	98	81
1	2	125	122
2	2	238	270
2	3	233	286
2	5	203	225
2	6	191	199
2	7	428	446
2	8	88	66
2	9	429	408
2	1	186	170
3	2	163	185
3	3	125	126
3	4	240	244
3	5	267	287
3	7	215	221
3	9	229	200
3	1	79	93
4	2	423	452
4	3	117	137
4	4	187	207
4	5	219	230
4	6	61	67
4	7	95	100
4	8	68	56
4	9	37	40
4	0	82	67
5	2	227	254
5	4	135	154
5	5	68	41
5	6	44	48
6	4	103	99
6	5	89	88
L=-1			
H	K	FO	FC
-6	4	103	91
-6	6	110	113
-5	3	92	106
-5	4	84	91
-5	5	71	82
-5	6	121	135
-5	8	95	87
-5	0	67	68
-4	3	281	263
-4	5	145	176
-4	1	87	74
-3	3	440	496
-3	5	253	208
-3	6	82	67
-3	7	65	85
-3	8	119	119
-3	9	58	49
-3	0	38	50
-3	1	67	73
-3	2	39	31
-3	3	55	47
-2	2	510	404
-2	3	70	45
-2	4	381	388
-2	5	76	70
-2	6	289	288
-2	7	45	53
-2	8	384	364
-2	9	43	23
-2	0	156	176
-2	1	54	63
-2	2	55	63
-1	3	234	223
-1	4	278	297
-1	5	44	46
-1	6	412	443
-1	7	115	151
-1	8	529	428
-1	9	41	36
-1	0	339	314
-1	2	116	110
0	3	545	540
0	5	214	264
0	6	156	204
0	7	91	106
0	8	184	185
0	9	115	114
0	0	163	163
0	1	117	118
0	3	79	73
1	3	971	887
1	6	90	108
1	7	83	107
1	8	77	69
1	9	101	116
1	0	50	56
1	1	118	124
1	2	47	46
1	3	97	87
2	5	39	62
2	6	249	276
2	7	104	99
2	8	257	278
2	9	49	64
2	0	121	129
2	1	100	97
2	2	67	68
3	2	161	211
3	4	276	340
3	5	151	158
3	6	368	358
3	7	144	180
3	8	274	279
3	0	171	166
3	2	68	75
4	2	121	141
4	3	228	256
4	4	218	253
4	5	60	68
4	6	226	244
4	7	36	35
4	8	154	147
4	0	95	97
5	2	90	106
5	3	153	209
5	4	99	123
5	6	76	97
5	8	72	78
6	1	123	134
6	3	145	158
6	5	87	79
L=-2			
H	K	FO	FC
-7	0	70	89
-7	2	106	91
-6	2	126	76
-5	0	37	46
-5	3	101	102
-5	5	181	172
-5	7	162	134
-5	9	105	98
-5	1	56	63
-4	2	290	254
-4	3	92	103
-4	5	113	141
-4	6	73	73
-4	7	166	149
-4	9	95	99
-4	1	69	58
-3	2	677	644
-3	4	316	323
-3	5	79	95
-3	6	33	39
-3	7	59	69
-3	0	100	85
-3	2	80	74
-3	4	69	56
-2	2	694	679
-2	3	102	154
-2	4	308	286
-2	6	180	177
-2	7	130	153
-2	9	92	105
-2	0	89	94
-2	1	53	43
-2	2	55	61
-2	4	70	50
-1	3	335	314
-1	4	159	177
-1	5	555	508
-1	6	209	212
-1	7	486	474
-1	9	286	292
-1	0	60	76
-1	1	201	187
-1	2	66	62
0	3	402	350
0	5	559	537
0	7	429	381
0	8	84	103
0	9	322	296
0	1	154	137
0	3	56	52
0	4	57	29
1	3	755	752
1	4	593	666
1	5	325	328
1	6	132	165
1	7	252	277
1	8	105	110
1	9	218	217
1	2	66	58
1	4	81	75
2	2	793	810
2	3	291	367
2	4	248	330
2	5	53	73
2	6	90	89
2	8	90	101
2	9	47	62
2	0	61	81
2	2	102	86
2	4	70	76
3	2	232	274
3	3	63	95
3	4	323	303
3	5	474	430
3	6	266	251
3	7	277	255
3	8	91	102
3	9	143	138
3	0	52	64
3	1	86	86
3	2	68	64
3	4	70	52
4	3	159	177
4	4	82	81
4	5	287	269
4	7	210	228
4	9	120	126
4	1	88	87
5	2	96	110
5	3	260	262
5	4	98	121
5	5	159	194
5	7	163	173
5	9	96	91
5	1	56	31
6	2	111	133
6	4	104	109
6	7	40	53
7	2	99	82
7	4	69	60
7	6	69	43
L=-3			
H	K	FO	FC
-7	1	116	81
-6	3	131	95
-5	2	106	94
-5	3	158	112
-5	4	124	109
-5	6	142	105
-5	8	102	90
-5	0	80	64
-4	2	176	140
-4	4	151	123
-4	6	221	166
-4	8	238	187
-4	0	157	127
-3	2	197	175
-3	3	346	296
-3	4	251	241
-3	5	116	123
-3	6	214	178
-3	8	198	168
-3	0	114	91
-3	1	63	49
-3	3	66	50
-2	2	220	173
-2	3	562	562
-2	4	464	448
-2	5	213	189
-2	6	178	138
-2	7	50	41
-2	8	74	78
-2	9	110	98
-2	1	113	88
-2	3	65	68
-1	3	383	389
-1	4	243	238
-1	5	244	237
-1	6	463	392
-1	7	64	72
-1	8	77	60
-1	0	103	93
-1	1	82	88
-1	2	43	37
-1	3	78	61
0	4	574	595
0	5	384	347
0	6	737	645
0	8	392	328
0	0	241	199
0	2	120	112
0	3	89	78
1	4	361	433
1	5	157	163
1	6	437	419
1	7	131	123
1	8	395	346
1	0	179	153
1	2	113	99
1	3	44	36
2	3	601	744
2	4	633	754
2	5	441	525
2	6	436	471
2	8	223	204
2	0	56	62
2	1	41	49
2	2	75	54
2	3	90	78
3	3	343	339
3	5	222	231
3	6	69	35
3	7	96	86
3	8	38	15
3	1	75	76
3	3	80	60
4	2	112	114
4	3	396	391
4	4	309	313
4	5	254	262
4	6	276	268
4	7	69	59
4	8	117	94
4	3	66	53
5	2	107	103
5	3	58	41
5	4	176	158
5	6	200	183
5	8	140	134
5	0	91	74
6	2	77	84
6	4	119	114
6	6	151	136
6	8	80	83
7	3	66	62
7	5	66	46
K=0			
H	L	FO	FC
-7	2	98	106
-7	6	75	81
-7	8	98	101
-6	2	155	180
-6	6	276	334
-6	10	58	68
-5	2	154	178
-5	4	153	175
-5	6	233	260
-5	8	159	180
-5	10	222	223
-5	14	102	104
-4	2	151	137
-4	4	281	291
-4	6	68	64
-4	8	408	408
-4	10	244	279
-4	14	175	179
-3	2	352	428
-3	4	335	394
-3	8	643	635
-3	10	132	138
-3	12	349	342
-3	16	79	77
-2	2	235	220
-2	4	502	491
-2	6	914	852
-2	8	427	410
-2	10	332	307
-2	12	171	132
-2	16	213	170
-1	2	602	651
-1	4	445	416
-1	6	750	732
-1	8	81	84
-1	10	478	497
-1	12	270	202
-1	14	108	99
-1	16	104	93
0	4	626	525
0	10	665	565
1	2	62	70
1	4	799	781
1	6	30	25
1	8	482	512
1	10	175	209
1	12	311	259
1	14	111	120
2	2	655	690
2	4	594	539
2	6	230	255
2	8	406	392
2	12	261	231
2	14	66	38
3	0	195	186
3	2	644	645
3	4	114	137
3	6	317	351
3	10	116	125
3	12	121	116
4	0	473	546
4	2	297	327
4	4	233	229
4	6	49	62
4	10	142	147
5	0	238	280
5	4	195	242
5	6	65	61
5	8	107	101
6	2	65	73
6	4	151	155
K=1			
H	L	FO	FC
-7	3	97	103
-7	7	106	126
-7	11	61	55
-7	13	60	49
-6	4	79	65
-6	5	112	118
-6	7	189	211
-6	9	30	44
-6	11	121	134
-6	15	81	83
-5	3	28	37
-5	4	74	84
-5	5	331	380
-5	9	220	224
-5	11	116	123
-5	12	41	39
-5	15	118	107
-4	1	284	297
-4	2	67	74
-4	3	279	311
-4	5	277	239
-4	6	88	95
-4	7	153	173
-4	8	44	45
-4	9	407	380
-4	11	67	70
-4	12	56	47
-4	13	192	185
-4	15	42	58
-4	17	82	68
-3	1	300	317
-3	3	379	423
-3	4	87	110
-3	5	197	195
-3	6	158	206
-3	7	604	599
-3	8	66	92
-3	9	264	260
-3	11	150	154
-3	13	195	151
-3	17	151	135
-2	1	463	465
-2	2	164	113
-2	3	477	486
-2	5	219	223
-2	6	324	255
-2	7	812	763
-2	8	190	210
-2	9	67	92
-2	10	66	71
-2	11	443	369
-2	12	183	156
-2	13	54	67
-2	15	101	107
-2	17	123	111
-1	4	274	226
-1	5	506	497
-1	6	247	200
-1	7	329	324
-1	8	171	123
-1	9	309	267
-1	10	80	58
-1	11	466	414
-1	12	216	166
-1	15	207	166
0	3	168	115
0	4	111	99
0	5	516	521
0	7	78	50
0	8	116	114
0	9	599	567
0	11	358	308
0	13	196	190
0	15	66	81
0	16	61	39
1	2	268	209
1	3	642	661
1	4	306	273
1	5	384	361
1	7	259	238
1	9	464	472
1	11	84	82
1	12	27	26
1	13	141	157
1	15	52	57
1	16	53	35
2	0	268	269
2	1	188	207
2	2	96	98
2	3	880	878
2	4	106	136
2	5	55	70
2	6	75	57
2	7	442	472
2	10	110	117
2	11	120	148
2	13	127	115
3	0	228	280
3	1	737	804
3	2	53	73
3	3	290	341
3	4	133	166
3	5	284	321
3	7	77	110
3	9	64	48
3	11	211	186
3	13	61	60
3	15	74	67
4	0	105	142
4	3	77	88
4	4	112	137
4	5	180	227
4	6	81	102
4	7	77	75
4	9	124	130
4	11	86	103
5	1	109	133
5	5	148	174
5	9	86	101
6	5	61	73
K=2			
H	L	FO	FC
-7	6	48	65
-7	8	107	119
-7	12	48	69
-6	5	56	85
-6	6	171	194
-6	10	122	118
-6	12	81	72
-6	14	67	45
-6	16	68	66
-5	4	232	267
-5	5	133	159
-5	6	157	155
-5	7	126	128
-5	8	30	43
-5	10	193	191
-5	11	87	98
-5	12	54	47
-5	14	112	116
-5	16	58	59
-4	4	355	394
-4	7	240	245
-4	8	271	253
-4	10	154	172
-4	11	76	63
-4	12	51	42
-4	14	164	145
-4	17	75	60
-4	18	83	75
-3	4	156	185
-3	5	200	220
-3	6	144	166
-3	7	115	121
-3	8	541	564
-3	9	100	117
-3	10	51	67
-3	11	113	109
-3	12	329	298
-3	15	53	50
-3	16	85	74
-3	18	75	66
-2	1	127	85
-2	3	337	311
-2	4	294	310
-2	5	230	214
-2	6	727	737
-2	8	390	368
-2	9	97	91
-2	10	287	263
-2	11	51	46
-2	12	207	204
-2	13	74	87
-2	15	81	80
-2	16	156	132
-1	5	538	541
-1	6	701	648
-1	8	125	139
-1	9	223	216
-1	10	320	304
-1	11	226	213
-1	12	189	195
-1	13	97	107
-1	14	177	142
-1	16	111	96
0	5	132	117
0	6	268	238
0	7	252	223
0	8	306	258
0	9	147	150
0	10	463	442
0	11	155	143
0	14	192	173
0	16	56	45
0	17	58	45
0	18	83	67
1	4	444	457
1	5	520	517
1	6	186	172
1	7	188	224
1	8	479	477
1	10	223	220
1	11	88	114
1	12	117	125
1	14	118	115
1	15	56	35
1	16	33	32
1	18	68	53
1	18	68	53
2	6	205	230
2	8	240	241
2	10	65	49
2	11	120	103
2	12	132	152
2	14	32	49
2	15	67	45
2	16	68	53
3	4	91	95
3	5	115	146
3	6	332	393
3	9	81	67
3	10	154	156
3	12	113	92
3	13	47	47
4	4	133	151
4	6	152	178
4	9	46	55
4	10	141	136
5	4	112	134
5	5	93	95
5	6	94	83
5	7	67	62
5	8	82	86
6	4	83	103

Solution of the Structures

For each structure, coordinates for copper were obtained from a three-dimensional Patterson synthesis and successive structure-factor calculations and Fourier syntheses revealed the positions of all non-hydrogen atoms; full-matrix least-squares refinement of all atomic coordinates, individual isotropic thermal parameters, and individual layer scale factors was continued until no parameters showed any significant change.

For Cu(PIA), refinement of the 55 variable parameters converged to a conventional R value ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.100; Table I lists the final structure parameters and Table II lists the observed and calculated structure factors.

For Cu(EIA), refinement of the 49 variable parameters converged to a conventional R value of 0.089: Table III lists the final structure parameters and Table IV lists the observed and calculated structure factors.

In the structure factor calculations, the scattering factors tabulated by Ibers[15] were employed for all atoms. Computations were carried out on the Burroughs 5500 computer and the Univac 1108 com-

Table III. Final Positional and Thermal Parameters for Cu(EIA).

Atom	x	y	z	B, A^2
Cu1	0.0493(2)	0.0915(2)	0.1619(5)	2.57(6)
O2	0.0797(13)	−0.0418(12)	0.1405(19)	2.29(32)
C3	0.1435(22)	−0.0629(22)	0.2716(35)	3.21(60)
C4	0.2166(22)	0.0114(24)	0.2783(34)	2.93(58)
N5	0.1652(18)	0.1035(18)	0.2758(28)	3.06(44)
C6	0.1994(22)	0.1750(22)	0.3575(35)	3.18(55)
C7	0.2878(23)	0.1767(23)	0.4474(39)	3.93(71)
C8	0.1531(22)	0.2622(21)	0.3442(44)	3.35(56)
C9	0.0710(23)	0.2798(21)	0.2560(36)	3.08(55)
C10	0.0288(28)	0.3774(30)	0.2435(48)	5.21(86)
O11	0.0198(16)	0.2198(15)	0.1735(32)	4.08(47)

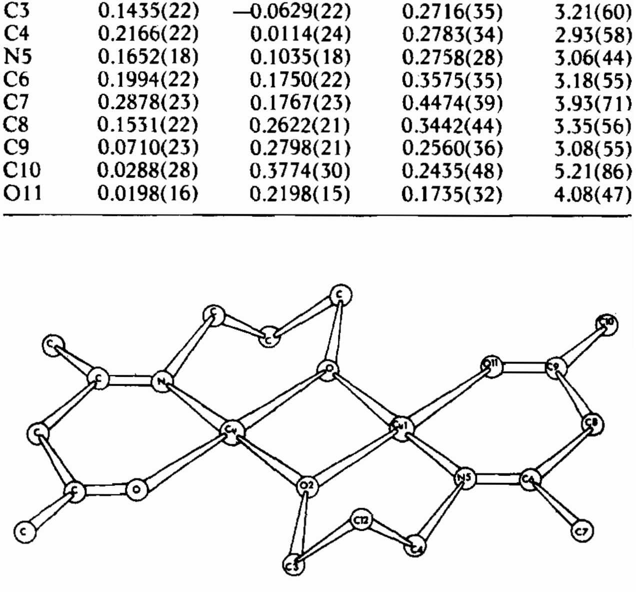

Figure 1. The molecular structure of Cu(PIA).

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

Table IV Observed and Calculated Structure Factors (Electrons × 10) for Cu(EIA).

K=0

H	L	FO	FC
6	0	1020	938
8	0	809	822
16	0	312	250
2	1	588	546
3	1	811	797
4	1	585	538
5	1	452	462
6	1	823	846
7	1	773	756
8	1	560	566
10	1	809	902
12	1	469	445
15	1	194	116
16	1	241	168
0	2	2909	2957
1	2	293	320
2	2	951	794
3	2	988	905
5	2	460	475
6	2	434	470
7	2	107	128
8	2	186	148
9	2	666	713
11	2	491	468
13	2	263	272
15	2	195	162
16	2	139	119
17	2	276	268
1	3	1645	1681
3	3	978	901
5	3	652	656
6	3	398	283
7	3	818	934
10	3	122	152
11	3	126	78
12	3	130	104
15	3	239	224
0	4	726	675
2	4	534	484
3	4	853	921
5	4	227	206
6	4	492	434
7	4	237	189
8	4	421	387
9	4	466	470
11	4	453	388
13	4	272	258
14	4	194	161
15	4	137	128
1	5	206	186
2	5	339	376
3	5	208	154
4	5	271	313
7	5	178	204
8	5	222	216
10	5	458	412
12	5	333	362
15	5	134	55
0	6	808	887
2	6	512	507
6	6	453	435
8	6	266	289
9	6	189	112
14	6	185	134
1	7	597	660
2	7	189	172
3	7	189	172
4	7	232	248
5	7	300	258
6	7	190	161
7	7	270	254
10	7	233	253
12	7	261	245
5	8	233	249
9	8	260	273
11	8	210	251
1	9	416	438
3	9	130	80
5	9	128	133
7	9	173	210
0	10	397	372

K=1

H	L	FO	FC
4	0	837	681
5	0	747	723
6	0	975	808
7	0	1134	1073
8	0	682	670
9	0	412	361
10	0	189	191
11	0	163	71
12	0	343	346
14	0	264	258
15	0	237	197
16	0	140	110
17	0	143	134
3	1	271	268
4	1	508	490
5	1	612	708
6	1	768	702
7	1	413	426
8	1	463	425
9	1	575	601
11	1	691	684
12	1	173	167
13	1	180	136
15	1	238	235
16	1	141	112
17	1	203	196
1	2	1107	1100
2	2	765	651
3	2	803	753
4	2	508	470
5	2	632	599
6	2	667	658
7	2	422	420
8	2	391	381
9	2	190	155
12	2	396	359
16	2	246	262
2	3	1190	1134
3	3	407	450
4	3	220	285
5	3	600	606
6	3	812	933
7	3	434	439
8	3	477	500
9	3	404	406
11	3	125	105
12	3	129	57
13	3	133	133
14	3	137	131
15	3	198	192
16	3	202	173
1	4	761	918
2	4	286	326
3	4	438	456
4	4	471	416
5	4	480	484
6	4	282	287
7	4	501	533
8	4	242	302
10	4	476	520
12	4	299	284
14	4	140	114
16	4	202	204
2	5	340	357
3	5	513	516
4	5	122	145
5	5	246	304
6	5	250	284
9	5	414	424
11	5	333	354
13	5	140	184
15	5	201	145
1	6	686	813
3	6	184	183
5	6	263	296
6	6	188	225
7	6	464	469
8	6	234	249
10	6	195	154
14	6	141	120
2	7	306	353
3	7	275	279
4	7	194	170
5	7	239	233
6	7	277	276
7	7	139	161
8	7	198	166
9	7	243	265
11	7	244	215
13	7	197	152
3	8	200	217
4	8	141	187
5	8	141	155
6	8	141	167
8	8	141	104
10	8	242	276
2	9	200	191
6	9	139	171
7	9	138	135

K=2

H	L	FO	FC
5	0	690	651
6	0	1336	1244
7	0	1334	1400
9	0	462	442
11	0	173	125
13	0	544	524
15	0	418	412
16	0	265	229
4	1	453	427
5	1	604	595
6	1	602	671
7	1	364	383
8	1	522	526
9	1	192	223
10	1	553	471
11	1	176	170
12	1	226	235
14	1	286	247
15	1	148	140
16	1	217	219
17	1	224	213
3	2	224	225
4	2	820	842
5	2	208	214
6	2	525	503
7	2	557	568
8	2	192	158
9	2	497	477
11	2	446	443
12	2	190	160
13	2	198	211
15	2	261	257
16	2	220	188
17	2	159	130
3	3	172	137
4	3	547	504
5	3	568	582
6	3	591	608
7	3	614	668
8	3	763	856
10	3	225	192
11	3	190	171
12	3	197	203
13	3	144	103
14	3	366	382
15	3	153	125
16	3	273	238
17	3	160	123
2	4	682	789
3	4	202	191
4	4	673	734
5	4	421	425
6	4	658	601
7	4	441	416
8	4	185	224
9	4	465	494
10	4	138	101
11	4	284	308
12	4	206	169
13	4	299	264
15	4	222	180
17	4	161	137
3	5	524	564
4	5	296	247
5	5	501	505
7	5	239	210
8	5	199	189
10	5	292	316
11	5	149	118
12	5	215	206
15	5	159	110
16	5	227	166
2	6	426	371
3	6	202	160
4	6	203	156
5	6	323	347
6	6	462	471
7	6	511	432
8	6	211	210
9	6	302	282
10	6	153	105
13	6	275	248
15	6	227	180
3	7	304	356
4	7	152	148
5	7	307	343
6	7	267	270
7	7	219	198
8	7	270	304
10	7	223	180
12	7	226	158
14	7	159	140
16	7	154	151
2	8	274	263
4	8	275	267
5	8	159	188
11	8	160	167
1	9	229	191
6	9	161	205
8	9	159	181

K=3

H	L	FO	FC
6	0	1298	1290
7	0	658	626
8	0	1108	1069
12	0	290	312
13	0	306	274
14	0	574	545
16	0	412	382
17	0	161	172
6	1	551	491
7	1	607	562
8	1	207	200
9	1	470	446
10	1	333	321
11	1	176	131
12	1	131	119
13	1	338	349
15	1	301	248
16	1	271	221
17	1	162	122
18	1	236	203
6	2	685	629
7	2	232	215
8	2	383	394
9	2	234	244
10	2	246	199
11	2	183	124
12	2	191	183
13	2	141	117
14	2	208	206
15	2	153	90
16	2	275	191
17	2	231	194
4	3	345	365
5	3	445	464
6	3	481	477
7	3	818	872
8	3	171	161
9	3	591	618
10	3	293	334
11	3	193	145
12	3	245	287
13	3	509	506
15	3	415	376
16	3	161	107
3	4	772	782
5	4	568	646
6	4	432	458
8	4	396	454
9	4	136	101
10	4	140	167
11	4	204	170
12	4	210	196
14	4	315	298
16	4	165	183
4	5	597	632
5	5	135	144
6	5	276	243
7	5	281	341
8	5	202	212
9	5	253	261
10	5	149	116
4	6	207	201
5	6	296	312
6	6	335	374
8	6	343	430
9	6	155	165
12	6	230	214
14	6	289	330
16	6	169	157
4	7	352	376
5	7	224	196
6	7	225	195
7	7	321	347
8	7	162	110
9	7	163	207
3	8	286	315
5	8	166	176
7	9	241	219

L=0

H	K	FO	FC
3	3	420	332
4	4	317	358
5	5	356	347
8	8	182	153
9	9	157	143
10	10	437	489
11	11	512	503
12	12	438	398

L=2

H	K	FO	FC
2	2	853	794
3	3	911	903
4	4	586	581
5	5	480	502
6	6	331	317
7	7	595	572
8	8	374	437
9	9	198	214
10	10	167	196
11	11	241	223
12	12	208	169

L=4

H	K	FO	FC
4	4	470	494
5	5	231	190
6	6	386	319
7	7	565	544
8	8	324	328
9	9	235	213
10	10	207	238
11	11	206	269

L=6

H	K	FO	FC
4	4	196	197
6	6	164	161
7	7	267	324
8	8	118	119
9	9	166	166
10	10	227	277

L=8

H	K	FO	FC
4	4	165	257
5	5	164	192

Table V Comparison of Intramolecular distances and Angles in Cu(PIA) and Cu(EIA).

Atoms	Intramolecular Distances, Å Cu(PIA)	Cu(EIA)
Cu1-Cu1′	3.026(6)	3.006(8)
Cu1-Cu1″		3.259(8)
Cu1-O2	1.86(1)	1.98(2)
Cu1-O2′	1.92(1)	2.00(2)
Cu1-O2″		2.32(2)
Cu1-O11	1.96(2)	1.91(2)
Cu1-N5	1.83(1)	1.90(2)
C9-O11	1.31(2)	1.30(4)
O2-C3	1.43(2)	1.40(3)
C4-N5	1.49(3)	1.53(4)
N5-C6	1.28(2)	1.30(3)
C9-C10	1.52(3)	1.54(5)
C6-C7	1.53(2)	1.45(4)
C8-C9	1.42(3)	1.39(4)
C6-C8	1.40(3)	1.43(4)
C4-C12	1.53(3)	
C3-C12	1.56(3)	
C3-C4		1.51(4)

Atoms	Cu(PIA)	Cu(EIA)
Cu1-O2-Cu1′	106.4(6)	97.8(8)
O2-Cu1-O2′	73.6(6)	81.4(8)
O2-Cu1-O2″		81.8(7)
O2′-Cu1-O2″		81.3(7)
O2-Cu1-N5	99.6(6)	86.0(10)
O2″-Cu1-N5		120.3(8)
O2′-Cu1-N5	173.1(6)	153.1(8)
O2′-Cu1-O11	91.8(6)	98.4(9)
N5-Cu1-O11	95.0(7)	95.0(11)
Cu1-O2-C3	129.4(12)	107.5(17)
Cu1′-O2-C3	124.2(12)	118.6(16)
N5-C4-C3		106.3(24)
O2-C3-C4		109.4(25)
N5-C4-C12	114.4(20)	
O2-C3-C12	108.2(16)	
C3-C12-C4	116.2(22)	
Cu1-N5-C4	119.6(14)	110.9(17)
C4-N5-C6	117.7(19)	120.1(24)
Cu1-N5-C6	122.7(15)	128.8(23)
N5-C6-C8	120.3(19)	119.1(27)
C6-C8-C9	125.8(19)	126.7(29)
C8-C9-O11	120.6(19)	126.7(30)
Cu1-O11-C9	129.4(15)	122.9(21)

puter; programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy ORFLS and ORFFE least-squares and function and error programs, and various locally written programs.

Description of the Structures

The molecular geometry and the atomic numbering scheme for Cu(PIA) and Cu(EIA) are shown in Figures 1 and 2, respectively; Table V summarizes some of the intramolecular distances and angle of the two compounds. Table VI presents the equations of selected planes and the distances of atoms from these planes.

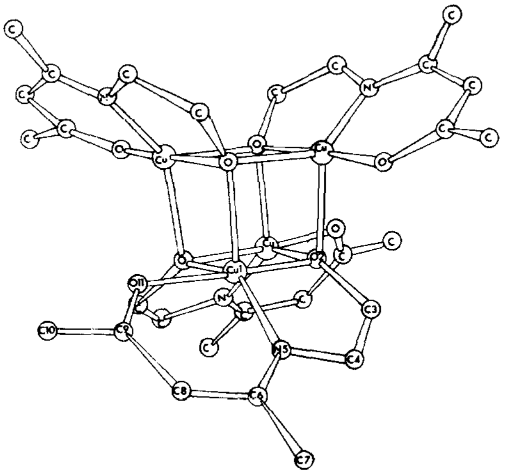

Figure 2. The molecular structure of Cu(EIA).

Cu(PIA). The dimeric complex contains a central four-membered ring which, because of an inversion center at the center of the ring, is exactly planar;

Table VI. Equations of Atomic Planes and Distances (Å) of Atoms from these Planes.

(a) Equation of the Plane of the Four-Membered Ring (Cu1, O2, Cu1′, O2′) of Cu(PIA): [a]

$$0.620\ X + 0.739\ Y - 0.264\ Z = 0.000$$

Cu1	0.000	C4	0.044	C9	−0.082
O2	0.000	N5	−0.028	C10	−0.106
Cu1′	0.000	C6	−0.120	O11	−0.006
O2′	0.000	C7	−0.230	C12	0.235
C3	0.018	C8	−0.215		

(b) Equation of the Best Least-Squares Plane[b] of the Acetylacetonate Chelate Ring (N5, C6, C8, C9, C10, O11) of Cu(PIA): [a]

$$0.620\ X + 0.762\ Y - 0.186\ Z = 0.212$$

N5	0.014	C9	0.009	O2	−0.197
C6	0.019	C10	0.026	C3	−0.167
C7	0.001	O11	−0.020	C4	0.074
C8	−0.049	Cu1	−0.090	C12	0.658

(c) Equation of the Best Least-Squares Plane[b] of the Acetylacetonate Chelate Ring (N5, C6, C7, C8, C9, C10, O11) of Cu(EIA):

$$0.499\ X + 0.196\ Y - 0.844 = -0.329$$

N5	0.040	C9	−0.012	O2	−0.119
C6	−0.036	C10	0.041	C3	0.082
C7	0.026	O11	−0.021	C4	0.133
C8	−0.037	Cu1	−0.098		

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

in addition, the coordination sphere of each copper ion is planar as indicated by the fact that none of the coordinated atoms are out of the plane defined by the four-membered ring by more than 0.03 Å. The coordination around the bridging oxygen is also essentially planar, with the carbon bonded to the oxygen only 0.02 Å out of the plane of the four-membered ring.

In addition to the four-membered ring, there are two six-membered chelate rings consisting of copper, oxygen, nitrogen, and three carbon atoms. One of these chelate rings contains the carbons from the acetylacetone and will be referred to hereafter as the unsaturated chelate ring; the other six-membered chelate ring contains the carbons from the aminopropanol and will be referred to hereafter as the saturated chelate ring.

The five carbon atoms of each unsaturated chelate ring are essentially coplanar (the greatest deviation of any of the five atoms from their least-squares plane is 0.05 Å) and that plane forms a dihedral angle of *ca.* 10° with the plane of the four-membered ring; since the two unsaturated chelate rings of the dimer are related by inversion, they are bent in opposite directions from the plane of the copper-oxygen ring. The carbon-carbon bond distances within the chelate ring do not differ by as much as their standard deviations.

The saturated chelate ring, as expected, is considerably bent. As indicated above, the carbon bonded to the oxygen is in the plane of the four-membered ring; the carbon bonded to the nitrogen is only slightly out of that plane (0.12 Å); the other carbon of the ring is the only atom of the entire structure that causes the dimer to deviate significantly from planarity– it is 0.74 Å from the plane on the side opposite the unsaturated chelate ring of the same ligand.

Cu(EIA). The tetrameric complex, like the previously reported acetylacetone-mono-(*o*-hydroxyanil)-copper(II),[4] can be thought of as two dimers held together by Cu–O bonds. In the previous structure, one dimer was displaced with respect to the other so that there were only two such interactions per tetramer; in the ethanolimine complex, one dimer is rotated 90° with respect to the other so that there are four Cu–O interactions. The Cu–Cu distance between « dimers » (3.26 Å) is longer than the Cu–Cu distance within the « dimer » (3.01 Å).

The dimer does not contain an inversion center as did the propanolimine complex but has a two-fold axis instead. The four-membered ring of copper and oxygen is, thus, not required to be planar; the extent of bending of the ring is indicated by the dihedral angles between the two Cu–O–Cu planes, *ca.* 14°, and between the two O–Cu–O planes, *ca.* 12°. The carbon bonded to the bridging oxygen also shows the effect of bending the ring; the Cu–O–Cu plane makes a dihedral angle of 59.6° with the Cu–O–Cu plane.

The coordination around copper is somewhat distorted but is essentially bipyramidal with the two oxygens of one chelate ligand in axial positions; the nitrogen of the same ligand and the oxygens of two other ligands of the tetramer occupy equatorial positions. As in the μ_4-oxo complexes,[16,17] the copper is displaced out of the equatorial plane (0.23 Å). The angles between the groups in the equatorial plane (81, 120 and 153°) are not indicative of square pyramidal coordination (90, 90, 180°) nor of trigonal bipyramidal coordination (all 120°).

The tridentate ligand forms a six-membered ring (unsaturated chelate ring) and a five-membered ring (saturated chelate ring). The unsaturated chelate ring is virtually identical to that found in the Cu(PIA) structure; in the saturated chelate ring, the carbon bonded to the oxygen is considerably out of the plane of the rest of the chelate ring.

Discussion

Although their formulas differ by only one carbon atom, the room temperature magnetic moments of Cu(PIA) and Cu(EIA) are markedly different, 0.41 and 1.87 B.M., respectively. The sub-normal moment of Cu(PIA) is characteristic of a large number of oxygen-bridged copper(II) complexes; the moment of Cu(EIA), although normal for an isolated copper(II) ion, is unsual for an oxygen-bridged copper(II) complex-previously reported normal magnetic moments in oxygen-bridged copper(II) complexes have been in μ_4-oxo complexes.[16,17] in dimers of bis-chelates,[18] and

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(16) J. A. Bertrand and J. A. Kelley, *J. Am. Chem. Soc.*, *88*, 4746 (1966); J. A. Bertrand, *Inorg. Chem.*, *6*, 495 (1967).

(17) B. T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, *1*, 209 (1967).

(18) J. A. Bevan, D. P. Graddon, and J. F. McConnell, *Nature*, 199, 373 (1963).

in the dimeric complex of N,N′-ethylene-bis(salicylideneiminato).[19]. Because of the difference in magnetic properties, a comparison of the structures of Cu(PIA) and Cu(EIA) should provide additional evidence as to the mechanism of the spin-exchange interaction in oxygen-bridged complexes.

In both complexes, the unsaturated chelate ring is essentially planar and contains C-C bonds of equal length (1.40, 1,42, and 1.39, 1.43); this is different from the results obtained[4] for the complex of copper(II) and the Schiff base formed from acetylacetone and *o*-aminophenol in which the chelate ring C–C distances were considerably different (1.32, 1.49 Å). The conclusion that there is no delocalization of the π-electrons in this portion of the ligand is not supported by the present results.

The principal difference in the two structures is the coordination of the bridging oxygens - in Cu(PIA) coordination about oxygen is planar while in Cu(EIA) coordination around oxygen is tetrahedral; the difference can be understood in terms of the chelate rings formed. In order for the coordination around a bridging oxygen to be planar (sp^2 hybridization), the Cu1–O2–C3 angle must be at least 120° (since the Cu1–O2–Cu1′ angle is considerably less than 120°, the two Cu–O–C angles for each oxygen must average more than 120° to maintain planarity). In the case of Cu(PIA), it is possible to have Cu–O–C angles of 129° *and* square-planar coordination around copper without any steric strain; however, the same arrangement in Cu(EIA), because of the smaller chelate ring, would be extremely strained. The strain can be relieved to some extent by a change to sp^3 hybridization of the oxygen orbitals, thus decreasing the Cu–O–C angle within the chelate ring; this angle is 108° in Cu(EIA).

With the change in hybridization of the oxygen, the ethanolimine ligand makes it impossible to have a planar four-membered metal-oxygen ring *and* square-planar coordination of the metal; in Cu(EIA), the four-membered ring is slightly bent (the two Cu–O–Cu planes show a dihedral angle of 14°) and the coppers are five-coordinate. In the corresponding nickel complex,[20] square-planar coordination of the metal is maintained but the four-membered ring shows much greater bending (the two Ni–O–Ni planes show a dihedral angle of 40°).

In the case of the planar arrangement, three of the four outer orbitals of each bridging oxygen (2s, $2p_x$, and $2p_y$) are used for α-bonding and the fourth orbital ($2p_z$) is available for π-bonding with the copper d_{xz}, d_{yz} orbitals; in the case of the non-planar dimer, the fourth orbital does not have π-symmetry and it enters into σ-bonding, forming the cubane-type structure.

It seems significant that for all of the oxygen-bridged copper(II) complexes with normal magnetic moments at room temperature, structure studies[16-19] have indicated tetrahedral hybridization of the outer orbitals of oxygen and π-bonding is not possible.

Although the oxygen $2p_z$ orbital and the copper d_{xz}, d_{yz} orbitals of Cu(PIA) have the correct symmetry for forming π-type molecular orbitals,[8] the assumption that dπ-pπ overlap would raise the π* orbital above the $d_{x^2-y^2}$ orbital– a condition necessary if the π-interaction is to account for the difference in magnetic properties of these two compounds– may be questioned. However, a comparison of the two structures raises questions about other possible explanations of their magnetic properties. Super-exchange involving the copper $d_{x^2-y^2}$ orbitals (σ-overlap) has been suggested; although the Cu–O bonds within the four-membered rings of the two structures differ by approximately 0.10 Å, it seems unlikely that such a small difference could lead to the dramatic difference in magnetic properties; furthermore, the Cu–O distances in $CuCl_2(PyO)$,[5] which has a low magnetic moment, are longer than those in Cu(EIA). Metal-metal σ-bonding has been suggested for some vanadyl complexes[21] of Schiff's bases and is also a possibility in the copper compounds; the fact that the Cu–Cu distances in Cu(EIA) and Cu(PIA) are almost identical rules against that possibility. Metal-metal π-bonding (through d_{z^2} orbitals) can be questioned on the same basis.

The remaining possibility is a π-interaction involving the oxygen pπ orbitals and the copper dπ orbitals. The six orbitals in C_i symmetry can be combined to form three molecular orbitals of A_g symmetry and three molecular orbitals of A_u symmetry. One molecular orbital of A_g symmetry and one of A_u symmetry will be strongly bonding, one orbital of each symmetry will be anti-bonding, and the remaining two orbitals (on the metal ions) will be essentially non-bonding. Of the ten electrons available, eight will fill the bonding and non-bonding orbitals and there will be two electrons for the pair of anti-bonding orbitals. Although the two anti-bonding orbitals are not degenerate, the energy difference would be expected to be small and, thus, would give rise to a singlet ground state and a low-lying triplet state. Furthermore, since the copper dπ orbitals also overlap with the π-system of the chelate ring and since the different symmetries of the two anti-bonding orbitals cause them to interact differently with the chelate π system, the energy difference would be affected by changes in the chelate π-system; in the case of the pyridine N-oxide complexes, the interaction of the oxygen π-orbital with the pyridine π-system would also affect the energy difference. In studies of copper complexes of substituted pyridine N-oxides[7] and in studies of both copper[6] and vanadyl[21] complexes of Schiff's bases formed from substituted salicylaldehydes and substituted o-aminophenols, some correlation between J (the energy difference between the pair of anti-bonding orbitals) and the resonance substituent constants has been observed.

The same explanation has been given previously[8] (D_{2h} symmetry was assumed) but omission of the pair of d_{xy} orbitals from the final molecular orbital diagram resulted in an incorrect filling of orbitals; in D_{2h} symmetry, the highest filled level should be the b_{1u} anti-bonding orbital derived from the d_{xz}, d_{yz} orbitals of the coppers.

The low magnetic moments of the vanadyl com-

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(19) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).
(20) J. A. Bertrand and C. E. Kirkwood, to be published.
(21) A. P. Ginsberg, E. Koubek, and H. J. Williams, *Inorg. Chem.*, *5*, 1656 (1966).

plexes were previously explained by assuming a direct overlap of d_{xy} orbitals; however, if the above π-bonding explanation is correct, the lowest lying d-orbital would be one of the non-bonding π-orbitals. Although labelled non-bonding, the pair of orbitals is not degenerate and the interaction of the orbitals with chelate π-orbitals of different symmetries would lead to a slight energy difference consistent with the observed values of J.

It should be pointed out that the oxygen-bridged copper(II) complexes which have normal moments at room temperature may exhibit spin-exchange at lower temperatures; such effects have been observed in the μ_4-oxo complexes[22] and in Cu(EIA).[23] Although spin-exchange through a pi-mechanism is not possible for such complexes, other mechanisms (which give rise to smaller splittings) are still possible.

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[22] A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, 154th Meeting, American Chemical Society, Chicago, Illinois, September, 1967, Abstracts of Papers, O-118.

[23] A. P. Ginsberg, Private communication.