Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia, 30332, U.S.A.

Sub-Normal Magnetic Moments in Copper (II) Complexes: Five-Coordinate Copper in an Oxygen-Bridged Dimer

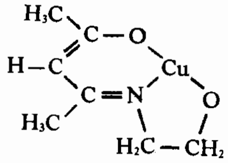
J. A. Bertrand, J. A. Kelley, and J. L. Breece

Received December 23, 1969

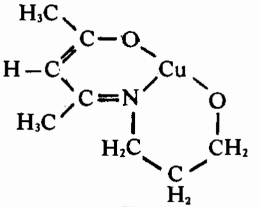
The preparation, structure, and properties of a dimeric copper(II) compound, chloro-N-(2-hydroxypropyl)-salicylaldimino copper(II), are reported. The compound, which has a magnetic moment of 1.1 B.M., crystallizes as brown, monoclinic crystals ($a = 8.56(1)$ Å; $b = 12.35(2)$ Å; $c = 10.31(2)$ Å; *and* $\beta = 98.43(3)^\circ$) *of space group* $P2_1/c$ *with two dimers per unit cell; the calculated density of 1.71 g/cm^3 agrees well with the observed density of 1.69 g/cm^3. A total of 644 unique, non-zero reflections were collected (four-circle diffractometer); least-squares refinement with anisotropic temperature parameters for copper and chlorine resulted in a conventional R value of 0.089. Each copper is five-coordinate (distorted trigonal bipyramid) and the phenolic oxygens are the bridging groups. The four-membered copper-oxygen ring is planar with a Cu–Cu distance of 3.294(7) Å; coordination of the bridging oxygen is also planar. The low magnetic moment is attributed to a π-interaction delocalized over the four-membered ring. For the atoms bonded to copper the bond distances and bond angles are: Cu–N (axial), 2.18(2) Å; Cu–O (axial), 2.22(1) Å; Cu–O (equatorial), 1.78(1) and 2.24(2) Å; Cu–Cl (equatorial), 2.12(1) Å; N–Cu–O (axial), 168.9(6)°; O–Cu–O (equatorial), 123.4(7)°; Cl–Cu–O (equatorial), 126.2(5)° and 110.1(4)°.*

Introduction

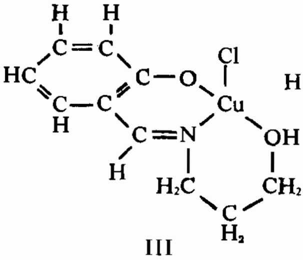
Oxygen-bridged copper(II) complexes with sub-normal magnetic moments have been known[1] for some time and there has been considerable discussion of the mechanism of spin-exchange in such complexes. Recently, we reported[2,3] structures for oxygen-bridged copper(II) complexes with normal and sub-normal magnetic moments. Cu(EIA), I, was found to have a normal moment and the structure study showed the compound to be tetrameric with tetrahedral coordination about oxygen and a distorted five-coordinate arrangement about copper; Cu(PIA), II, was found to have a very low magnetic moment and the structure study showed the compound to be dimeric with planar three-coordination about oxygen and planar four-coordination about copper. The difference in magnetic moments was attributed to the different oxygen coordinations–in the planar three-coordinate arrangement, one orbital is available for delocalized π-bonding with the copper(II) ions. However, the possibility that the difference in magnetic properties is related to the difference in coordination about copper(II) could not be ruled out on the basis of the two structures reported. We have now prepared and determined the structure of an oxygen-bridged copper(II) complex with a sub-normal magnetic moment in which the copper is five-coordinate. Chloro-{N-(2-hydroxypropyl)salicylaldimino}copper(II), III, (hereafter abbreviated Cu(SalPA)Cl), contains a Schiff's base ligand prepared by the condensation of salicylaldehyde and 3-amino-1-propanol; the previously reported[4] compound, IV, contained the dianion of the same ligand.



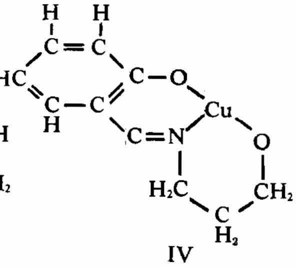
I



II



III



IV

Experimental Section

Preparation. The ligand was prepared by mixing 0.01 mole (7.5 g) of 3-amino-1-propanol with 0.01 mole (12.2 g) of salicylaldehyde; the product was dissolved in methanol and added to a hot, methanol solution containing 0.005 moles (6.72 g) of anhydrous copper(II) chloride. The light brown solid was filtered and recrystallized from methanol.

---

(1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, *64*, 99 (1964).
(2) J. A. Bertrand, J. A. Kelley, and C. E. Kirkwood, *Chem. Comm.*, 1329 (1968).
(3) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, *3*, 30 (1969).
(4) S. Yamada, Y. Kuge, and K. Yamanouchi, *Inorg. Chim. Acta*, *1*, 139 (1967).

Anal. Calcd. for $CuC_{10}H_{11}NO_2Cl$: Cu, 22.92; C, 43.33; H, 4.40; N, 5.05. Found: Cu, 22.93; C, 43.13; H, 4.36; N, 5.04.

Magnetic Susceptibility. The magnetic susceptibility of the compound, 465×10^{-6} cgsu/g.at. of copper, was determined by the Gouy method at 25°C using $HgCo(CNS)_4$ as a calibrant. A correction for diamagnetism (133×10^{-6} cgsu/g.at. of copper) was made using published atomic values.[5] The value of μ_{eff} was found to be 1.1 B.M.

Structure Determination. Suitable crystals for single-crystal studies were obtained by recrystallization of the powdered material from methanol to which a few drops of hydrochloric acid had been added; a needle-like crystal of approximate dimensions $0.10\times0.50\times0.12$ mm was mounted on a glass fiber along the long dimension (unique axis) of the crystal; optical examination and precession photographs indicated a monoclinic cell; the absence of *h0l* reflections for $l = 2n+1$ and *0k0* reflections for $k = 2n+1$ uniquely defined the space group as $P2_1/c$.

The crystal was transferred to an automated Picker four-circle diffractometer; six reflections were used to refine cell parameters by a least-squares procedure. The cell parameter obtained are $a = 8.56(1)$ Å,[6] $b = 12.35(2)$ Å, $c = 10.31(2)$ Å, $\beta = 98.43(3)°$, and $V = 1078$ Å^3 (25°C, molybdenum radiation, $\lambda = 0.7107$ Å).

The calculated density of 1.71 g/cm^3 for four formula units per unit cell agrees well with the observed density of 1.69 g/cm^3 measured by the flotation method using a mixture of carbon tetrachloride and methylene iodide.

The x-ray intensity measurements were made, using the same crystal as used for the cell measurements, with molybdenum radiation. The insensities were measured with a scintillation counter mounted 21 cm. from the crystal; the intensities were collected by the θ-2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° min^{-1}. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary background counts of 20 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Previously calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10,000 counts/second. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A total of 1256 reflections were collected with periodic checks of two standard reflections. After about one-fifth of the data had been collected the intensities of the standard reflections increased sharply by about ten percent; the intensities of the standards were very constant before that point and they were very constant at the increased value through the remainder of the data collection. Separate scale factors were used for the two portions of data. Corrected intensities (CI) were obtained by subtracting three times the actual measured background from the total integrated peak count (CT),

$$CI = CT - 0.5(t_c/t_b)(bgd1+bgd2)$$

The corrected intensities were assigned standard weviations according to the formula[7]

$$\sigma(I) = [CT+0.25(t_c/t_b)^2(bgd1+bgd2)]^{1/2}$$

where t_c is the scan time and t_b is the counting time of each background (either bgd1 or bgd2). For the refinement, a total of 644 reflections for which $\sigma(I)/CI$ was less than 0.05 were employed. The intensities were corrected for Lorentz and polarization effects but were not corrected for absorption (calculated linear absorption coefficient is 23 cm^{-1}); the maximum error in the structure factors due to the omission of the absorption correction was less than 5%.

The coordinates of the copper and chlorine atoms were found from a three-dimensional Patterson synthesis. After three cycles of full-matrix least-squares refinement, the conventional R value was 0.24. From an electron density map phased on these atoms, the remaining non-hydrogen atoms were located. Four cycles of full-matrix least-squares refinement resulted in an R value of 0.14. At this point a weighting scheme[7] based on counting statistics ($w=4(CI)/\sigma(I)^2$) was introduced and least-squares refinement, minimizing $w(|F_o|-|F_c|)^2$, was continued; varying all atomc coordinates, individual isotropic temperature factors and two scale factors gave an R_1 ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.13 and an R_2 ($\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|^2\}^{1/2}$) of 0.12. Anisotropic temperature factors were then introduced for the copper and chlorine atoms; the refinement was continued, varying all parameters, until no parameter showed any significant change. The final values are $R_1=0.089$ and $R_2=0.081$. The ratio of the second scale factor (data after the increase in intensity) to the first scale factor is 0.908 and reflects the increase in intensity. The final observed and calculated structure factors are listed in Table I and the final structure parameters are listed in Table II.

Computations were carried out on the Burroughs 5500 computer and on the Univac 1108 computer; programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy ORFLS and ORFEE least-squares and function and error programs, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[8] were employed for all atoms. No corrections were made for anomalous dispersion.

Discussion

The sub-normal magnetic moment of Cu(SalPA)Cl (1.1 B.M.) indicates considerable spin-exchange at room temperature; the moment is somewhat higher than that found for Cu(PIA), 0.41 B.M.

---

(5) B. N. Figgis and J. Lewis in « Modern Coordination Chemistry », J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

(6) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least-significant digits.

(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(8) J. A. Ibers in « International Tables for X-ray Crystallography », Vol. 3, the Kynoch Press, Birmingham, England, 1962.

Table I. Observed and Calculated Structure Factors (Electrons ×10) for Cu(SalPA)Cl

	L=-8		
H	K	FO	FC
1	0	46	47
2	0	27	22
3	0	37	48
4	0	32	21
5	0	44	40
6	0	44	46
7	0	33	24
1	2	25	24
4	2	28	20
5	2	30	24
6	2	31	30
7	2	29	26
2	3	26	30
5	3	28	30
7	4	30	21
1	5	53	59
2	5	40	31
3	5	48	52
4	5	38	31
5	5	29	26
7	5	28	6
1	7	52	52
2	7	38	32
3	7	36	32
4	7	41	42
1	9	30	21
4	9	29	21
	L=-7		
H	K	FO	FC
1	1	86	92
2	1	52	62
6	1	29	31
1	2	41	45
2	2	30	44
5	2	29	23
6	2	33	38
1	3	44	44
2	3	41	42
3	3	40	40
7	3	28	23
2	4	39	43
3	4	39	44
5	4	31	35
6	4	30	25
3	5	39	45
1	6	33	34
2	6	38	34
3	6	46	49
4	6	35	36
6	6	27	17
5	7	27	18
3	8	31	24
4	8	51	67
5	8	31	18
	L=-6		
H	K	FO	FC
1	0	30	31
2	0	70	74
3	0	64	71
4	0	51	52
5	0	59	73
6	0	30	13
2	1	29	30
3	1	33	32
4	1	25	20
1	2	62	67
2	2	76	82
3	2	47	47
4	2	34	38
5	2	30	23
3	3	42	47
4	3	27	21
1	4	82	88
2	4	53	53
3	4	30	27
1	5	41	38
2	5	39	41
6	5	27	14
7	5	36	40
1	6	28	24
1	7	34	36
2	7	25	23
4	7	27	31
6	7	30	26
7	7	33	37
1	8	28	24
4	8	29	27
4	9	32	32
	L=-5		
H	K	FO	FC
5	1	37	36
6	1	32	21
7	1	34	44
4	2	22	10
2	3	24	20
3	3	30	26
4	3	33	36
5	3	29	19
6	3	40	41
7	3	34	23
1	4	42	37
2	4	40	42
3	4	34	34
1	5	31	27
2	5	27	28
3	5	25	24
4	5	26	22
5	5	28	26
6	5	29	30
1	6	64	66
2	6	38	29
3	6	35	33
2	7	35	36
3	7	27	20
1	8	39	43
3	8	27	20
4	8	29	28
	L=-4		
H	K	FO	FC
7	0	27	17
4	1	40	38
5	2	29	23
6	2	26	18
7	2	31	27
3	3	49	49
4	3	48	47
5	3	31	30
4	4	29	25
5	4	42	41
6	4	38	40
7	4	33	34
4	5	25	17
5	5	39	38
6	5	35	32
7	5	33	35
1	6	24	21
1	7	36	37
2	7	33	30
3	7	28	20
4	7	33	28
5	7	34	33
6	7	36	39
7	7	29	22
2	8	27	22
1	9	52	55
2	9	56	61
3	9	48	50
4	9	37	40
5	9	34	33
6	9	28	21
	L=-3		
H	K	FO	FC
5	1	32	35
7	2	25	24
4	3	52	55
5	3	24	19
4	4	40	36
5	4	32	33
6	4	35	40
7	4	36	39
4	5	27	23
5	5	28	27
3	6	27	22
4	6	41	43
5	6	47	45
6	6	48	52
7	6	37	38
1	7	40	42
2	7	26	30
3	7	35	35
5	8	30	27
6	8	34	33
7	8	33	31
	L=-2		
H	K	FO	FC
5	0	38	42
6	0	40	44
7	0	34	35
7	1	34	35
5	2	58	62
6	2	58	64
7	2	26	22
7	3	39	40
4	4	86	89
5	4	77	82
6	4	44	46
3	6	24	18
5	6	35	33
1	7	50	52
2	7	25	23
3	7	24	24
4	7	28	25
1	8	40	41
5	8	29	24
1	9	58	64
2	9	56	57
3	9	45	42
4	9	34	33
5	9	28	23
6	9	30	27
7	9	36	36
	L=-1		
H	K	FO	FC
5	1	55	57
6	1	66	70
7	1	51	52
7	2	33	35
5	3	50	53
6	3	32	33
5	4	49	50
4	5	35	26
5	5	42	44
7	5	27	29
3	6	60	59
4	6	71	72
5	6	45	45
2	7	28	23
7	7	32	31
1	8	83	83
2	8	75	78
3	8	45	43
4	8	41	39
2	9	27	23
	L= 0		
H	K	FO	FC
6	0	62	68
6	1	40	41
6	2	31	28
5	3	52	53
6	3	45	46
5	4	29	28
4	5	64	62
5	5	52	52
2	7	107	105
3	7	76	80
4	7	54	55
5	7	31	28
6	7	29	26
7	7	29	25
0	8	41	36
1	8	31	27
2	8	29	27
4	8	48	47
1	9	27	23
3	9	42	43
5	9	30	29
6	9	46	52
7	9	45	49
	L= 1		
H	K	FO	FC
6	1	51	52
6	2	30	23
5	3	52	47
7	4	30	28
4	5	35	34
5	5	29	21
5	6	25	21
7	6	32	35
6	7	27	19
7	7	30	19
0	8	49	52
1	8	75	71
4	8	34	32
5	8	43	45
6	8	32	34
7	8	32	32
2	9	25	17
3	9	39	41
	L= 2		
H	K	FO	FC
6	0	116	123
7	0	64	67
5	2	43	42
6	2	67	69
7	2	56	59
5	3	46	40
6	3	30	24
5	4	25	22
7	4	42	40
4	5	70	63
7	5	32	29
4	6	50	50
5	6	42	43
2	7	46	42
3	7	71	64
4	7	60	59
0	8	43	43
1	8	27	19
4	8	40	40
5	8	35	32
6	8	31	23
0	9	50	55
1	9	29	27
3	9	26	22
4	9	33	25
	L= 3		
H	K	FO	FC
6	1	30	22
7	1	41	39
5	2	62	56
6	2	32	26
5	3	40	35
6	3	48	47
4	4	37	34
5	4	36	34
6	4	47	43
7	4	29	19
5	5	40	37
6	5	35	32
7	5	34	32
3	6	32	27
4	6	37	33
5	6	35	30
6	6	51	50
7	6	33	33
1	7	23	13
2	8	36	35
3	8	53	55
4	8	56	61
5	8	66	68
6	8	40	40
	L= 4		
H	K	FO	FC
5	0	68	64
6	0	33	25
5	2	38	34
2	3	30	20
3	3	41	35
4	3	45	37
5	3	30	26
6	3	28	21
7	3	36	28
0	4	94	98
1	4	81	82
2	4	65	57
3	4	41	37
0	5	52	52
1	5	42	40
2	5	55	48
4	5	31	29
5	5	51	49
6	5	64	65
7	5	52	56
2	6	30	27
3	6	36	33
4	6	39	35
0	7	33	33
1	7	29	26
4	7	40	40
5	7	45	46
6	7	50	52
7	7	37	40
0	8	29	21
3	8	26	18
2	9	29	26
3	9	37	35
4	9	42	40
5	9	37	34
	L= 5		
H	K	FO	FC
0	1	36	31
1	1	48	46
2	1	106	96
3	1	92	90
4	1	69	65
5	1	58	58
6	1	38	38
1	2	69	58
3	2	42	34
4	2	31	25
5	2	27	19
2	3	41	36
3	3	55	46
4	3	63	60
5	3	55	57
6	3	59	63
7	3	37	41
0	4	73	73
1	4	67	68
2	4	42	39
5	4	31	22
6	4	29	19
0	5	30	28
3	5	49	40
4	5	40	39
5	5	38	37
6	5	33	32
7	5	31	28
0	6	78	87
1	6	51	57
2	6	47	46
5	6	35	29
6	6	32	28
1	7	34	36
3	7	37	33
0	8	39	43
1	8	37	34
2	8	39	39
3	8	46	48
	L= 6		
H	K	FO	FC
5	0	41	36
7	0	57	67
2	1	42	39
3	1	47	36
4	1	26	17
1	2	32	27
4	2	55	49
5	2	39	38
6	2	36	38
7	2	38	43
0	3	29	23
1	3	63	64
2	3	65	65
3	3	54	49
4	3	43	38
0	4	69	69
1	4	49	48
3	4	43	36
4	4	63	61
6	4	51	54
0	5	36	33
1	5	26	23
2	5	35	34
3	5	28	25
4	5	32	27
5	5	30	31
6	5	41	39
0	7	34	39
1	7	40	39
2	7	42	44
3	7	41	41
5	7	46	46
6	7	31	27
3	8	28	23
4	8	33	27
0	9	39	42
1	9	55	62
2	9	63	70
3	9	40	48
4	9	32	33
5	9	30	24
	L= 7		
H	K	FO	FC
0	1	71	71
1	1	58	61
2	1	55	54
3	1	48	48
5	1	35	29
0	2	26	18
4	2	31	23
7	2	43	40
0	3	46	45
1	3	31	31
2	3	25	17
3	3	34	28
5	3	41	31
3	4	41	39
4	4	51	31
7	4	40	40
0	5	36	37
1	5	32	29
2	5	29	29
4	5	35	24
5	5	30	25
2	6	33	30
3	6	58	61
4	6	36	40
5	6	41	49
6	6	36	40
0	7	29	24
1	7	42	44
2	7	30	30
7	7	36	33
1	8	34	28
2	8	34	32
5	8	31	30
6	8	37	41
	L= 8		
H	K	FO	FC
0		47	49
1	0	63	61
2	0	51	53
3	0	31	28
4	0	37	39
6	0	42	34
2	1	27	20
3	1	31	25
0	2	31	21
1	2	41	39
2	2	42	41
3	2	48	50
4	2	47	48
5	2	48	44
6	2	35	30
1	3	26	16
2	3	27	17
3	3	37	31
7	3	37	35
2	4	32	28
3	4	47	50
4	4	48	47
5	4	58	59
6	4	31	25
0	7	38	36
1	8	29	23
0	9	38	41
1	9	32	31
2	9	31	30
6	9	38	41
7	9	38	40

Table II. Positional and Thermal[a] Parameters for Cu(SalPA)Cl

Atom	x	y	z	B,Å^2 or $\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$
Cu	−0.0489(3)	0.0291(3)	0.1447(3)	38(4)	29(2)	31(3)	14(4)	−36(2)	−6(3)
Cl	0.1070(7)	0.1362(5)	0.2596(6)	107(12)	19(6)	67(8)	−13(6)	−49(7)	4(5)
O2	−0.1208(15)	0.0428(13)	−0.0250(12)	1.7(5)					
C3	−0.2653(26)	0.0872(19)	−0.0463(22)	2.1(8)					
C4	−0.2764(25)	0.1008(19)	−0.1813(21)	1.8(7)					
C5	−0.4255(27)	0.1448(20)	−0.2096(22)	2.2(8)					
C6	−0.5425(28)	0.1681(20)	−0.1137(25)	2.6(8)					
C7	−0.5271(24)	0.1531(19)	0.0165(22)	1.9(8)					
C8	−0.3738(22)	0.1101(17)	0.0501(19)	0.8(6)					
C9	−0.3750(24)	0.1036(18)	0.1868(20)	1.5(7)					
N10	−0.2478(19)	0.0778(14)	0.2414(16)	1.5(6)					
C11	−0.2684(25)	0.0743(18)	0.3876(21)	1.9(8)					
C12	−0.2822(26)	−0.0454(23)	0.4444(23)	3.0(9)					
C13	−0.1302(25)	−0.1104(19)	0.4050(21)	2.0(8)					
O14	−0.0955(17)	−0.1163(13)	0.2635(15)	2.7(6)					

[a] Anisotropic temperature factors expressed as $\exp[(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

The structure, Figure 1, consists of dimeric units of Cu(SalPA)Cl with the phenolic oxygens bridging copper(II) ions; selected bond distances and bond angles are presented in Table III. The copper-copper distance in this compound (3.29 Å) is considerably longer than the 3.03 Å found for the dimer of Cu(PIA); it is comparable in length to the long copper-copper distance (3.26 Å) of Cu(EIA). The long copper-copper distance and the low magnetic moment of Cu(SalPA)Cl offer further support for the argument that direct interaction between the metal ions is not responsible for the sub-normal magnetic moments in these compounds.

The four-membered copper-oxygen ring is unsymmetrical with short copper-oxygen distance (1.78 Å) to the oxygen of the ligand chelated to the copper and a long copper-oxygen distance (2.22 Å) to the oxygen of the other ligand; in Cu(PIA), these distances were almost equal (1.86 and 1.92 Å).

The copper is five-coordinate and the coordination approaches a trigonal bipyramid with the nitrogen and the oxygen from the other ligand (02′) in the axial positions; the N–Cu–O2′ angle is 170° instead of the 180° required for a bipyramid. The copper is displaced 0.06 Å from the plane of the equatorial atoms (02,014,Cl) and the equatorial angles are 123, 126, and 110°. The copper-nitrogen distance (2.18 Å) is considerably longer than the copper-nitrogen distances in Cu,EIA), 1.90 Å, and in Cu(PIA), 1.83 Å. The Cu-014 distance, 2.24 Å, is considerably longer than

Table III. Selected Intramolecular Distances and Angles for Cu(SalPA)Cl

Atoms	Distances, Å
Cu1—Cu1'	3.294(7)
Cu1—Cl	2.115(6)
Cu—O2	1.78(1)
Cu1—O2'	2.22(1)
O2—O2'	2.31(3)
Cu1—N10	2.18(2)
Cu1—O14	2.24(2)
O2—C3	1.34(2)
C3—C4	1.39(3)
C4—C5	1.38(3)
C5—C6	1.53(3)
C6—C7	1.34(3)
C7—C8	1.41(3)
C3—C8	1.48(3)
C8—C9	1.41(3)
C9—N10	1.19(2)
N10—C11	1.54(3)
C11—C12	1.60(3)
C12—C13	1.63(3)
C13—O14	1.53(3)

Atoms	Angle, degrees
Cu1—O2—Cu1'	110.3(6)
O2—Cu1—O2'	69.7(6)
Cl—Cu1—O2	126.2(5)
Cl—Cu1—O2'	98.6(4)
Cl—Cu1—O14	110.1(4)
Cl—Cu1—N10	92.5(5)
O2'—Cu1—O14	99.6(6)
O2'—Cu1—N10	168.9(6)
O14—Cu1—N10	76.0(6)
O14—Cu1—O2	123.4(7)
N10—Cu1—O2	104.0(6)
Cu1—O2—C3	112.3(1.3)
Cu1'—O2—C3	137.2(1.2)
O2—C3—C4	98.0(1.9)
C4—C3—C8	133.1(2.0)
C8—C3—O2	128.9(1.9)
C3—C4—C5	100.6(2.1)
C4—C5—C6	127.6(2.1)
C5—C6—C7	129.8(2.2)
C6—C7—C8	104.4(2.0)
C7—C8—C3	123.9(1.9)
C7—C8—C9	97.1(1.8)
C3—C8—C9	139.0(1.8)
C8—C9—N10	110.2(2.0)
C9—N10—Cu1	125.4(1.6)
C11—N10—Cu1	130.7(1.7)
C9—N10—C11	103.9(1.8)
N10—C11—C12	114.1(1.7)
C11—C12—C13	105.0(1.8)

the copper-alcohol oxygen distances in Cu(EIA), 1.91 Å, and Cu(PIA), 1.96 Å, but in those structures the alcohol proton was removed and the alcohol oxygen was the bridging group. The Cu—O2 distance, 1.78 Å, is shorter than the shortest copper-oxygen distances in Cu(EIA), 1.91 Å, or in Cu(PIA), 1.86 Å. The copper-chlorine distance, 2.12 Å, is short in comparison to other structures[9] (2.2-2.4 Å).

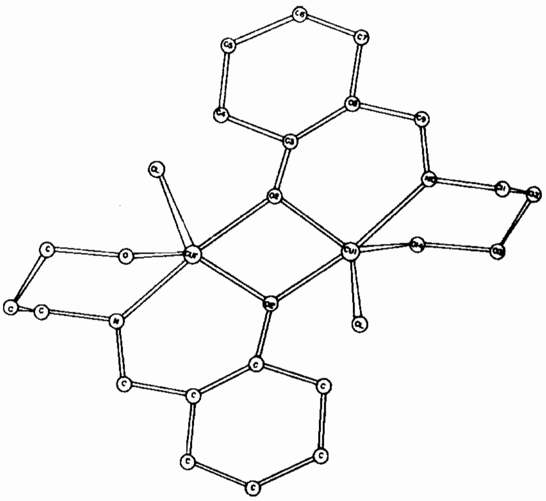


Figure 1. The molecular structure of Cu(SalPA)Cl

The coordination of copper in this structure is very similar to that found for copper(II) in Cu(EIA); the fact that the magnetic moments of the two compounds are very different suggests that the coordination of copper is not a major factor in the mechanism of spin-exchange.

The coordination about the bridging oxygen is essentially planar; the carbon (C3) bonded to the bridging oxygen is only 0.08 Å out of the plane of the two copper ions and the oxygens. A similar arrangement about the bridging oxygen was found in Cu(PIA) but not in Cu(EIA). As suggested previously, the planar coordination about the bridging oxygen is consistent with a π-mechanism for the spin-exchange.

Acknowledgments. This work was supported by NSF Grants GP-7406 and GP-8475. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged; the help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.

---

(9) J. A. Bertrand and J. A. Kelley, *Inorg. Chem.*, *8*, 1982 (1969).