structure, belonged to this class but that then its electrical behavior (ionic conductivity) was not explained. From the structure it seems that both types of conductivity should take place. Figure 5 shows the channels through which the Ni ions can move. However, because of differences in order of magnitude of electronic and ionic transference numbers, any ionic conductivity present is probably obscured.

Crystallographic Determination of Stereochemistry for the Triclinic and Tetragonal Modifications of a Bis-Bidentate Metal Complex, Bis(*N-tert*-butylpyrrole-2-carbaldimino)copper(II)[1]

BY CHIN HSUAN WEI[2]

The crystal structures of the triclinic and tetragonal modifications of a bis-bidentate copper complex, bis(*N-tert*-butyl-pyrrole-2-carbaldimino)copper(II), have been determined from three-dimensional single-crystal X-ray diffraction data which were measured photographically. The triclinic crystals belong to space group $P\bar{1}$ ($C_i{}^1$, No. 2) with $a = 7.49$ (1) Å, $b = 11.26$ (2) Å, $c = 11.73$ (2) Å, $\alpha = 81° 41'$ (15'), $\beta = 89° 38'$ (15'), $\gamma = 76° 16'$ (15'), and $Z = 2$. The tetragonal crystals possess $P4_12_12$ ($D_4{}^4$, No. 92) symmetry with $a = 9.89$ (2) Å, $c = 19.08$ (2) Å, and $Z = 4$. Both structures were solved by heavy-atom techniques and refined by the full-matrix least-squares method. The final reliability indexes are $R_F = 0.069$ and $R_{wF} = 0.056$ (1089 reflections) for the triclinic form and $R_F = 0.083$ and $R_{wF} = 0.070$ (504 reflections) for the tetragonal modification. The molecule ideally conforms to C_2 symmetry in the triclinic cell and possesses crystallographic C_2 symmetry in the tetragonal cell. The two molecular structures are similar, and the coordination around the copper atom may be described as distorted tetrahedral, with the dihedral angles of 61.3 (4) and 60.1 (9)° for the triclinic and tetragonal modifications, respectively, between the two coordination planes each defined by an MN₂ moiety. In each case, the M–N(pyrrole) bond distance [2.054 (8) Å for the former and 2.044 (14) Å for the latter] is approximately 0.12 Å longer than the M–N(azomethine) bond distance [1.939 (8) Å for the former and 1.922 (15) Å for the latter]. The interchelate N–Cu–N "bite" angles are 84.7 (4) and 85.4 (6)°, and the N···N bite distances are 2.69 (1) and 2.69 (2) Å for the triclinic and tetragonal modifications, respectively.

Introduction

Various four-coordinated copper(II) complexes, particularly those of salicylaldimines, have been reported and many of them have been subjected to two- or three-dimensional X-ray analyses.[3–11] The structural results reveal that most of these complexes are effectively square planar with only a few complexes exhibiting configurations which may be described as flattened or distorted tetrahedral. As an example,

bis(*N*-isopropylsalicylaldiminato)copper(II),[9] first reported as having a structure nearly isomorphous with that of the Ni(II) analog[12] whose structure was later determined as pseudotetrahedral,[13] has been shown to possess a dihedral angle of 59.7° between the two coordination planes each defined by Cu, N, and O atoms. Unlike the *n*-butyl analog, which is planar,[10] the *tert*-butyl analog[11] also has a distorted tetrahedral configuration with a dihedral angle of 53.6° between the two coordination planes defined as above. Recently, the molecule of bis(2,3-bipyridylamine)copper(II)[14] has also been shown to have a dihedral angle of 55.6° between the two CuN₂ coordination planes. It has been well recognized that steric interaction between the ligands is an important factor for a copper(II) complex to exhibit the configuration which deviates from planarity to varying degrees.

In 1966, Holm and his coworkers[15] reported that they had synthesized bis(*N-tert*-butylpyrrole-2-carbaldimino)metal(II) complexes where metal = cobalt, nickel, copper, and zinc (with the pyrrole–CH–N–*t*-Bu moiety as a ligand) and made extensive investigations of their chemistry. Structural analyses

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(2) Biology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

(3) (a) For a complete coverage up to about Dec 1964 see R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 110 (1966); (b) for the latest review on the stereochemistry of bis(chelate)metal(II) complexes, see R. H. Holm and M. J. O'Conner, *ibid.*, **14**, 241 (1971).

(4) To supplement in part the references given in ref 3a, the results of three-dimensional X-ray structural determinations of the bis(*N*-alkylsalicylaldiminato)copper(II) series alone have appeared in the literature since 1965 for alkyl = H,[5] CH₃,[6] C₂H₅,[7] *n*-propyl,[8] isopropyl,[9] *n*-butyl,[10] and *tert*-butyl.[11]

(5) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 680 (1966).

(6) D. Hall, S. V. Sheat, and T. N. Waters, *ibid.*, 460 (1968).

(7) (a) E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters *ibid.*, 251 (1967); (b) G. R. Clark, D. Hall, and T. N. Waters, *ibid.*, 2808 (1969).

(8) G. Bombieri, C. Panattoni, E. Forsellini, and R. Graziani, *Acta Crystallogr., Sect. B*, **25**, 1208 (1969).

(9) P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, **88**, 277 (1966).

(10) D. Hall, R. H. Summer, and T. N. Waters, *J. Chem. Soc. A*, 420 (1969).

(11) T. P. Cheeseman, D. Hall, and T. N. Waters, *ibid.*, 685 (1966).

(12) L. Sacconi and P. L. Orioli, *Ric. Sci.*, **32**, 645 (1962).

(13) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Crystallogr.*, **17**, 1159 (1964).

(14) J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc. A*, 1371 (1971).

(15) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

were performed for this series of complexes, and the results for the tetrahedral Co(II)[16a] (isomorphous with the zinc complex) and pseudotetrahedral Ni(II)[16b] complexes have been previously reported. As part of a systematic investigation of the structures of these complexes, we now present the study of the Cu(II) complex, which is found to exist in two crystalline modifications. A preliminary account of the structures has been given by Holm, *et al.*[15]

Experimental Section

Samples.—$(C_9H_{13}N_2)_2Cu^{II}$ was generously furnished by Professor R. H. Holm, University of Wisconsin (now at Massachusetts Institute of Technology). Suitable single crystals were obtained in two crystalline modifications from *n*-heptane solutions: a light green, needlelike form and a dark green, truncated tetragonal-pyramidal form. Examinations of their X-ray patterns revealed that the former was triclinic and the latter tetragonal.

Crystal Data. Triclinic Modification.—One of the crystalline modifications of $(C_9H_{13}N_2)_2Cu^{II}$ (mol wt 361.96) is triclinic with a reduced primitive unit cell of symmetry $P\bar{1}$ (C_i^1, No. 2)[17] and with cell parameters $a = 7.49$ (1) Å, $b = 11.26$ (2) Å, $c = 11.73$ (2) Å, $\alpha = 81° 41'$ (15'), $\beta = 89° 38'$ (15'), and $\gamma = 76° 16'$ (15') (lattice parameter errors were estimated on the basis of reproducibility of the measurements). The volume of the unit cell is 950 Å³. The observed density of 1.25 (2) g cm⁻³ (by the flotation method) is in agreement with the calculated value of 1.28 g cm⁻³ based on two $(C_9H_{13}N_2)_2Cu$ formula units per unit cell. The total number of electrons per unit cell, $F(000)$, is 382. All atoms occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[17]

Tetragonal Modification.—The second modification of the copper complex is tetragonal with $a = 9.89$ (2) Å and $c = 19.08$ (2) Å. The volume of a unit cell is 1868 Å³. The observed density of 1.28 (2) g cm⁻³ is close to the calculated value of 1.29 g cm⁻³ based on four formula units per unit cell; $F(000) = 764$. The systematic absences of $h00$ for h odd (and $0k0$ for k odd) and $00l \neq 4n$ indicate that the space groups are either $P4_12_12$ (D_4^4, No. 92) or $P4_32_12$ (D_4^8, No. 96).[18] The space group $P4_12_12$ was arbitrarily chosen for the refinement of the structure, since no selection of the correct enantiomer was possible with the relatively low-precision photographic data.[19]

Collection of X-Ray Data.—Intensity data were collected with zirconium-filtered Mo Kα radiation (λ 0.7107 Å) by the equi-inclination–Weissenberg and precession methods. Approximate dimensions of the crystals used were $0.43 \times 0.20 \times 0.09$ mm and $0.40 \times 0.26 \times 0.08$ mm for the triclinic modification and $0.65 \times 0.34 \times 0.22$ mm for the tetragonal modification. The crystals were mounted parallel to their longest dimensions (corresponding to the *a* axis in each case) in thin-walled glass capillary tubes. For the triclinic modification, $0kl$ through $4kl$ Weissenberg data and $h0l$, $h1l$, and $hk0$ precession data were collected from the the first crystal; $5kl$ through $7kl$ Weissenberg data were recorded from the second crystal. To eliminate errors due to spot compaction,[20] a full 360° range of Weissenberg data consisting of two separate sets of film packets was taken for each reciprocal-lattice level except $0kl$, and the intensities of only those reflections recorded on the top halves of the films were measured. In the case of the tetragonal modification, $0kl$ through $10,kl$ Weissenberg data and $hk0$, $h0l$, and $h1l$ precession data were collected. Cell parameters were determined from precession photographs at room temperature (24°) for both complexes. All intensities were estimated visually by comparison with

corresponding sets of standard spots and then corrected for Lorentz–polarization effects. For each complex, common reflections which appeared more than once were averaged and a whole set of observed diffraction maxima was merged to put them on a single relative scale. Thus a total of 1089 independent reflections were obtained for the triclinic complex, and a total of 504 for the tetragonal complex.[21] No allowance was made either for absorption or for extinction. The linear absorption coefficient of 11.9 cm⁻¹ for the triclinic complex gives μR_{max} values at 0.12 and 0.16 for the first and second crystals, respectively, whereas μ of 12.1 cm⁻¹ for the tetragonal complex results in a value of 0.21 for μR_{max}. For these values of μR_{max}, the variation of absorption correction factors with θ is not appreciable,[22] and the maximum variation due to absorption of the intensities on a given layer was estimated to be approximately 10%. Minimum observed intensities, I_o (min), were estimated for each reciprocal level, and variable weights were assigned to individual observed structure amplitudes, F_o, in the following way: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(min)$; $\sqrt{w} = 1.25I_o^2/F_oI_o(min)^2$ if $I_o < 4I_o(min)$.

Determination of Structures

Triclinic Modification.—A three-dimensional Patterson function, computed by the Blount program,[23] provided initial copper positional parameters which were refined by the least-squares refinement program.[24] A three-dimensional Fourier synthesis,[23] using phases calculated from the resulting refined parameters, successfully gave the positions for the remaining 22 nonhydrogen light atoms in the asymmetric unit. The subsequent refinement of the structure in which thermal motions of all nonhydrogen atoms were treated as isotropic yielded a conventional reliability index R_F, defined as $\Sigma|\Delta F|/\Sigma|F_o|$, of 0.099; with anisotropic thermal parameters assigned only to the copper atom, the R_F value was lowered to 0.090. A three-dimensional difference Fourier synthesis at this stage showed a positive peak of density 0.7 e/Å³ in the immediate vicinity of the copper atom; the remaining positive peaks ranged from 0.3 to 0.4 e/Å³ with the exception of one peak which had a density of 0.6 e/Å³. These values may be compared with a peak-height range of 3.8–5.9 e/Å³ observed for the 18 carbon atoms. All 26 independent hydrogen atoms were located from this map based on chemical grounds. Since an attempt to refine the positional parameters of these hydrogen atoms (with a fixed isotropic temperature factor of 7.0 Å² assigned to each atom) together with the positional and anisotropic thermal parameters for the nonhydrogen atoms was not successful, the positional parameters of the 26 hydrogen atoms were thereafter fixed, and only two different isotropic temperature factors were assigned to two types of hydrogen atoms in the final refinement (*i.e.*, one factor to those atoms attached to the ring system and the other to the atoms attached to the methyl carbons). At the end of four cycles, the R_F and R_{wF} (defined as $[\Sigma w|\Delta F|^2/\Sigma wF_o^2]^{1/2}$) values remained at 0.069 and 0.056, respectively. The parameter shifts were all less than 25% of the corresponding standard deviations. All least-squares refinements in this paper were based on the minimization of $\Sigma w|\Delta F|^2$, and the standard errors $\sigma(F_o)$ of the observations were related to the previously defined w values by the relation $\sigma(F_o) = 1/\sqrt{w}$. The standard deviation of an observation of unit weight, defined as $[\Sigma w|\Delta F|^2/(n - p)]^{1/2}$, where n is the number of observations and p the number of parameters fitted to the data set, was 1.01.

In this triclinic structure, as well as in the structure of the tetragonal complex, the atomic scattering factors used were those of Thomas and Umeda[25] for copper, those of Berghuis, *et al.*,[26]

(16) (a) C. H. Wei, *Inorg. Chem.*, **11**, 1100 (1972); (b) C. H. Wei and J. R. Einstein, *Acta Crystallogr., Sect. B*, in press.

(17) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 75.

(18) Reference 17: (a) p 182; (b) p 186.

(19) Any enantiomorphous pair can only be distinguished by a determination of absolute configuration using the anomalous scattering effect. See, *e.g.*, (a) M. J. Buerger, "Vector Space and Its Application in Crystal-Structure Investigation," Wiley, New York, N. Y., 1959, Chapter 9, pp 198–217; (b) M. J. Buerger, "Crystal-Structure Analysis," Wiley, New York, N. Y., 1960, pp 542–547.

(20) *Cf.* M. J. Buerger, "X-Ray Crystallography," Wiley, New York, N. Y., 1942, pp 227–229.

(21) Since the diffraction patterns of this complex possess a Laue symmetry of D_{4h}-$4/mmm$, only reflections corresponding to one-sixteenth of the reflection sphere are crystallographically independent. Reflections corresponding to one-eighth of the reflection sphere were collected and were averaged according to the $4/mmm$ Laue symmetry.

(22) "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, p 295.

(23) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

(24) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(25) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(26) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Crystallogr.*, **8**, 478 (1955).

TABLE I
POSITIONAL AND THERMAL PARAMETERS FOR $(C_9H_{13}N_2)_2Cu^{II}$ [a-c]

***** TRICLINIC MODIFICATION *****

ATOM	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	ISO EQUIV B, Å²
CU	0.4347(2)	0.2892(2)	0.2657(2)	220(3)	84(3)	63(2)	-19(2)	-3(2)	-8(2)	4.1
N(1)	0.6866(11)	0.1758(10)	0.3146(9)	237(24)	80(16)	67(11)	-10(14)	-17(13)	-1(12)	4.3
N(2)	0.3751(14)	0.2514(10)	0.4268(8)	247(23)	124(18)	52(9)	-23(16)	22(14)	-17(11)	4.7
C(1)	0.8515(14)	0.1529(14)	0.2400(13)	159(26)	84(20)	188(20)	29(17)	51(19)	10(19)	6.3
C(2)	0.8259(19)	0.0923(17)	0.1377(12)	468(42)	247(31)	88(14)	-104(27)	33(20)	-98(20)	8.2
C(3)	0.8840(16)	0.2865(15)	0.2016(13)	327(34)	205(20)	205(20)	-43(23)	42(19)	59(20)	8.5
C(4)	1.0237(14)	0.0798(13)	0.3134(11)	220(27)	138(21)	164(16)	10(18)	-11(16)	-28(17)	6.9
C(5)	0.6850(16)	0.1329(13)	0.4232(14)	269(33)	70(21)	124(18)	-52(19)	-17(21)	24(18)	5.3
C(6)	0.5208(17)	0.1669(16)	0.4848(12)	277(34)	127(23)	71(14)	-94(23)	32(20)	-17(16)	4.9
C(7)	0.4694(20)	0.1245(15)	0.5941(12)	392(38)	110(23)	115(17)	-3(23)	68(22)	-4(18)	6.9
C(8)	0.2937(23)	0.1873(17)	0.6077(12)	479(46)	127(25)	83(15)	-132(27)	72(22)	1(17)	6.6
C(9)	0.2402(15)	0.2658(15)	0.5038(13)	301(30)	139(24)	119(16)	-90(20)	99(21)	-30(18)	6.2
N(1*)	0.3261(11)	0.4746(12)	0.2071(12)	176(18)	133(21)	50(12)	-26(15)	-3(11)	-31(14)	4.2
N(2*)	0.3734(12)	0.2658(17)	0.1130(10)	166(22)	165(24)	79(15)	-63(19)	-15(14)	-29(18)	5.0
C(1*)	0.3273(14)	0.5770(19)	0.2677(12)	235(29)	146(26)	81(14)	-5(20)	27(16)	-43(20)	5.5
C(2*)	0.1706(16)	0.5858(14)	0.3551(11)	368(33)	172(24)	141(15)	-48(22)	65(20)	-46(18)	7.8
C(3*)	0.5130(14)	0.5491(13)	0.3289(10)	263(29)	158(23)	110(13)	-45(19)	-43(15)	-37(16)	6.2
C(4*)	0.2956(16)	0.7032(17)	0.1839(13)	345(34)	134(23)	155(18)	-33(22)	-37(20)	-26(21)	7.4
C(5*)	0.2752(16)	0.4840(16)	0.1035(17)	262(28)	91(23)	46(14)	-23(20)	-3(16)	-13(18)	4.1
C(6*)	0.2768(18)	0.3816(21)	0.0451(18)	163(29)	172(32)	82(20)	-38(24)	-3(20)	-48(24)	5.2
C(7*)	0.2146(16)	0.3521(26)	-0.0522(15)	222(30)	242(37)	77(18)	-97(29)	-0(18)	-25(26)	6.5
C(8*)	0.2610(21)	0.2231(22)	-0.0517(17)	304(33)	162(29)	123(22)	-123(26)	47(21)	-62(25)	6.3
C(9*)	0.3548(19)	0.1767(17)	0.0512(14)	347(34)	172(30)	36(14)	-54(25)	-20(17)	-39(18)	5.7

ATOM	x	y	z	B
H(5)	0.831	0.108	0.450	9(4)
H(7)	0.607	0.025	0.650	d
H(8)	0.180	0.195	0.667	d
H(9)	0.103	0.300	0.476	d
H(2A)	0.904	0.060	0.060	13(5)
H(2B)	0.700	0.104	0.125	e
H(2C)	0.803	0.030	0.196	e
H(3A)	1.022	0.288	0.242	e
H(3B)	0.857	0.290	0.288	e
H(3C)	0.784	0.345	0.165	e
H(4A)	1.133	0.050	0.255	e
H(4B)	1.000	-0.013	0.338	e
H(4C)	1.060	0.133	0.363	e
H(5*)	0.185	0.575	0.080	e
H(7*)	0.193	0.433	-0.095	e
H(8*)	0.250	0.151	-0.120	e
H(9*)	0.400	0.080	0.088	e
H(2A*)	0.217	0.638	0.388	e
H(2B*)	0.217	0.505	0.400	e
H(2C*)	0.050	0.593	0.328	e
H(3A*)	0.533	0.637	0.387	e
H(3B*)	0.600	0.547	0.280	e
H(3C*)	0.533	0.448	0.375	e
H(4A*)	0.320	0.745	0.238	e
H(4B*)	0.140	0.705	0.168	e
H(4C*)	0.390	0.698	0.128	e

***** TETRAGONAL MODIFICATION *****

ATOM	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å²
CU	0.5438(2)	0.4562	5/8	67(2)	67	27(1)	-18(5)	-9(2)	-9	3.1
N(1)	0.5317(17)	0.5597(16)	0.5325(6)	60(18)	135(22)	30(4)	-54(22)	4(9)	-18(9)	4.0
N(2)	0.4698(15)	0.3067(17)	0.5733(7)	34(16)	170(28)	34(6)	15(22)	-22(11)	-16(10)	4.3
C(1)	0.5669(18)	0.7031(19)	0.5157(9)	102(30)	103(25)	42(7)	-48(26)	27(13)	26(13)	4.7
C(2)	0.7176(21)	0.7177(28)	0.5024(13)	94(37)	157(39)	103(12)	31(27)	24(17)	44(17)	8.3
C(3)	0.5156(18)	0.7848(18)	0.5769(7)	111(30)	121(24)	17(5)	-16(23)	-5(10)	-23(9)	3.8
C(4)	0.4877(16)	0.7532(18)	0.4485(9)	104(30)	170(30)	32(6)	-12(24)	11(10)	29(12)	5.1
C(5)	0.4829(15)	0.4798(27)	0.4858(9)	42(26)	207(44)	43(6)	43(6)	14(10)	34(14)	5.3
C(6)	0.4419(18)	0.3450(20)	0.5048(10)	15(20)	140(30)	40(7)	22(22)	-1(12)	-29(15)	3.9
C(7)	0.3986(18)	0.2355(27)	0.4637(10)	91(25)	174(34)	40(7)	-13(28)	14(13)	-30(16)	5.4
C(8)	0.3839(21)	0.1275(22)	0.5131(11)	126(30)	140(32)	46(10)	-34(28)	-8(14)	-54(16)	5.7
C(9)	0.4266(20)	0.1734(19)	0.5766(10)	101(29)	74(22)	49(8)	-53(25)	9(13)	-11(11)	4.7

ATOM	x	y	z	B
H(5)	0.469	0.507	0.434	f
H(7)	0.363	0.245	0.413	f
H(8)	0.353	0.055	0.488	f
H(9)	0.438	0.125	0.638	f
H(2A)	0.788	0.815	0.491	g
H(2B)	0.768	0.675	0.555	g
H(2C)	0.768	0.655	0.471	g
H(3A)	0.555	0.888	0.602	g
H(3B)	0.413	0.770	0.619	g
H(3C)	0.570	0.738	0.631	g
H(4A)	0.548	0.828	0.444	g
H(4B)	0.523	0.698	0.406	g
H(4C)	0.405	0.743	0.474	g

[a] Standard deviations of the least significant figures are given in parentheses in all tables and in the text. [b] The hydrogen atoms are numbered according to the carbon atoms to which they are attached. [c] The form of the anisotropic temperature factor ($\times 10^4$) is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Equivalent isotropic temperature factors for nonhydrogen atoms were calculated from the corresponding thermal parameters and unit cell parameters by the relation $B = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab \cos \gamma + 2\beta_{13}ac \cos \beta + 2\beta_{23}bc \cos \alpha)$: see W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959). [d] The isotropic temperature factor was set equal to that for H(5), which was adjusted. [e] The isotropic temperature factor was set equal to that for H(2a), which was adjusted. [f] Assigned isotropic temperature factor of 8.0 Å². [g] Assigned isotropic temperature factor of 10.0 Å².

for carbon and nitrogen, and those tabulated by Ibers[27] for hydrogen. The constants[28] $\Delta f' = 0.3$ and $\Delta f'' = 1.4$ were employed in the correction of the calculated structure factors for the anomalous scattering of the copper atom for the triclinic modification. However, only the real dispersion corrections were applied for the tetragonal modification.[29,30]

Tetragonal Modification.—Of a total of 504 independent reflections observed, 71 have a condition $h = k$. For computational purposes,[31] 433 additional reflections were generated from the averaged original set of data by interchanging h and k indices for the corresponding hkl reflections with $h \neq k$. This gave rise to a total of 937 reflections on the basis of D_{2h}-*mmm* Laue symmetry.

(27) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1A.

(28) (a) C. H. Dauben and D. H. Templeton, *Acta Crystallogr.*, **8**, 841 (1955); (b) D. H. Templeton in ref 27, p 215, Table 3.3.2C.

(29) Since the observed intensities were obtained by averaging two quantities for each pair of reflections hkl and khl, the refinement could have been carried out with the minimization of function $\Sigma w[|F_{o,av}| - |F_c|]^2$, where a valid *calculated* value of $|F_c|$ is defined[30] as $\{[F']^2 + |F''|^2\}^{1/2}$ in which $|F'|$ stands for the sum of the structure factor amplitudes due to nonanomalous scattering atoms and the real component of the copper atom, and $|F''|$ is the imaginary component due to the copper scattering factor. Hence in the actual refinement based on F, with $|F_c| = |F'|$, errors of relative magnitude $|F''|^2/2|F'|^2$ have been neglected—a procedure which was deemed justifiable in view of the small anomalous scattering effect and the low precision of the data.

(30) (a) A. L. Patterson, *Acta Crystallogr.*, **16**, 1255 (1963); (b) S. W. Hawkinson, C. L. Coulter, and M. L. Greaves, *Proc. Roy. Soc., Ser. A*, **318**, 143 (1970).

(31) Due to limitations imposed by the program used,[28] Patterson and Fourier syntheses were performed on the basis of an orthorhombic space group $P2_12_12_1$, using the 937 reflections comprised of both hkl and khl data.

Since there are four copper atoms per unit cell, they are required to be at the special fourfold set of positions (4a).[18a] This was confirmed by an inspection of the intensity data which revealed that there were only nine mostly weak reflections (014, 018, 01,16, 022, 026, 02,14, 034, 062, and 06,10) with $2k + l$ even or $\neq 4n$ for $0kl$. These nine reflections thus would be entirely due to the contributions of the light atoms which are located in pairs at the eightfold set of general positions (8b).[18a]

A three-dimensional Patterson function was computed on the basis of D_{2h} orthorhombic symmetry from the 937 intensities.[31] Two vectors having high peak values and appearing on Harker sections $(U, V, 1/4)$ and $(U, V, 1/2)$ gave the x and y coordinates for the basic copper atom. A choice was arbitrarily made to define the space group as $P4_12_12$ (*vide supra*), and the coordinates of the basic copper atom were initially assigned as $x = 0.55$, $y = 0.45$, and $z = 5/8$ (fixed). For the purpose of computational convenience, the origin of the unit cell was chosen to be located at an intersection of a twofold screw axis in the c direction and one-eighth below a twofold axis which is perpendicular to $(1\bar{1}0)$ planes.[32] The resulting unit cell possesses three twofold screw axes located at $(1/4 b, 1/4 c)$, $(1/4 a, 0c)$, and $(0a, 0b)$ in the a, b, and c directions, respectively.

(32) The z coordinates of atoms were chosen so that the origin of the unit cell given in ref 18a is shifted down by $1/8$ in the z direction. The consequence of this translation is that the basic copper atom is now positioned at $5/8z$ instead of at $3/4z$ on a diagonal twofold axis in the $[1\bar{1}0]$ direction of the unit cell. The special fourfold set of positions (4a) thus obtained are x, $1 - x$, $5/8$ (basic); $1 - x$, x, $1/8$; $x - 1/2$, $x - 1/2$, $7/8$; $1/2 - x$, $3/2 - x$, $3/8$. The general eightfold set of positions (8b) are x, y, z (basic): $-x, -y, 1/2 + z$; $1/2 - y, 1/2 + x, 1/4 + z$; $1/2 + y, 1/2 - x, 3/4 + z$; $y, x, 3/4 - z$; $-y, -x, 1/4 - z$; $1/2 - x, 1/2 + y, -z$; and $1/2 + x, 1/2 - y, 1/2 - z$. The subsequent calculations are invariant to these positional transformations.

TABLE II
INTERATOMIC DISTANCES (Å) AND INTERMOLECULAR ANGLES (DEG) WITH STANDARD DEVIATIONS[a]

BOND	TRICLINIC	TETRAGONAL	ANGLE	TRICLINIC	TETRAGONAL
CU–N(1)	2.044(11)	2.044(14)	N(1)–CU–N(2)	84.7(5)	85.4(6)
CU–N(1*)	2.068(13)		N(1*)–CU–N(2*)	84.6(7)	
	2.056(AV)			84.7(AV)	
CU–N(2)	1.949(10)	1.922(15)	N(1)–CU–N(1*)	137.7(4)	
CU–N(2*)	1.922(13)		N(1)–CU–N(1')		133.4(9)
	1.936(AV)		N(1)–CU–N(2*)	108.6(6)	
N(1)–C(1)	1.50(1)	1.50(2)	N(2)–CU–N(1*)	108.7(6)	
N(1*)–C(1*)	1.44(2)			109.2(AV)	
	1.47(AV)		N(1)–CU–N(2)		107.5(6)
N(1)–C(5)	1.30(1)	1.29(2)	N(2)–CU–N(2*)	142.1(5)	
N(1*)–C(5*)	1.26(2)		N(2)–CU–N(2)		148.1(9)
	1.28(AV)		CU–N(1)–C(5)	108.8(8)	108.2(12)
C(5)–C(6)	1.42(2)	1.44(3)	CU–N(1*)–C(5*)	107.6(13)	
C(5*)–C(6*)	1.42(2)			108.2(AV)	
	1.42(AV)		CU–N(2)–C(6)	109.7(8)	110.4(13)
C(6)–C(7)	1.39(2)	1.40(2)	CU–N(2*)–C(6*)	111.4(15)	
C(6*)–C(7*)	1.35(2)			110.6(AV)	
	1.37(AV)		N(1)–C(5)–C(6)	119.2(12)	120.0(15)
C(7)–C(8)	1.36(2)	1.43(3)	N(1*)–C(5*)–C(6*)	124.1(16)	
C(7*)–C(8*)	1.41(2)			121.7(AV)	
	1.39(AV)		N(2)–C(6)–C(5)	117.3(12)	115.7(16)
C(8)–C(9)	1.40(2)	1.36(2)	N(2*)–C(6*)–C(5*)	111.5(17)	
C(8*)–C(9*)	1.37(2)			114.4(AV)	
	1.39(AV)		C(6)–N(2)–C(9)	105.0(10)	103.9(13)
N(2)–C(9)	1.35(1)	1.39(2)	C(6*)–N(2*)–C(9*)	105.2(12)	
N(2*)–C(9*)	1.35(2)			105.1(AV)	
	1.35(AV)		N(2)–C(6)–C(7)	110.1(11)	112.1(19)
N(2)–C(6)	1.37(1)	1.39(2)	N(2*)–C(6*)–C(7*)	106.5(17)	
N(2*)–C(6*)	1.46(2)			108.3(AV)	
	1.42(AV)		N(2)–C(9)–C(8)	111.4(11)	111.9(16)
C(1)–C(2)	1.50(2)	1.52(3)	N(2*)–C(9*)–C(8*)	113.0(16)	
C(1*)–C(2*)	1.53(2)			112.2(AV)	
	1.53(AV)		C(6)–C(7)–C(8)	107.5(12)	103.9(16)
C(1)–C(3)	1.58(1)	1.51(2)	C(6*)–C(7*)–C(8*)	111.0(18)	
C(1*)–C(3*)	1.51(2)			109.3(AV)	
	1.55(AV)		C(9)–C(8)–C(7)	105.9(11)	107.8(17)
C(1)–C(4)	1.55(2)	1.58(2)	C(9*)–C(8*)–C(7*)	104.2(17)	
C(1*)–C(4*)	1.58(2)			105.1(AV)	
	1.57(AV)		CU–N(2)–C(9)	144.8(10)	145.6(13)
			CU–N(2*)–C(9*)	141.6(14)	
C(5)–H(5)	1.10	1.03		143.2(AV)	
C(7)–H(7)	1.41(MAX)	1.04	C(5)–C(6)–C(7)	132.4(15)	131.3(20)
C(8)–H(8)	1.09	0.92(MIN)	C(5*)–C(6*)–C(7*)	142.0(22)	
C(9)–H(9)	1.04	1.26		137.2(AV)	
C(2)–H(2A)	1.14	1.20	CU–N(1)–C(1)	125.9(8)	139.3(11)
C(2)–H(2B)	0.93	1.20	CU–N(1*)–C(1*)	126.9(10)	
C(2)–H(2C)	0.95	0.99		126.4(AV)	
C(3)–H(3A)	1.15	1.19	C(5)–N(1)–C(1)	125.2(11)	121.5(16)
C(3)–H(3B)	0.93	1.30(MAX)	C(5*)–N(1*)–C(1*)	125.1(16)	
C(3)–H(3C)	0.93	1.25		125.2(AV)	
C(4)–H(4A)	1.09	0.95	N(1)–C(1)–C(2)	114.2(11)	110.8(18)
C(4)–H(4B)	1.10	1.04	N(1*)–C(1*)–C(2*)	107.9(13)	
C(4)–H(4C)	0.98	0.96		111.1(AV)	
C(5*)–H(5*)	1.08	1.10(AV)	N(1)–C(1)–C(3)	103.5(11)	105.3(13)
C(7*)–H(7*)	0.95		N(1*)–C(1*)–C(3*)	106.9(12)	
C(8*)–H(8*)	1.24			105.2(AV)	
C(9*)–H(9*)	1.09		N(1)–C(1)–C(4)	110.2(11)	110.8(15)
C(2*)–H(2A*)	0.88		N(1*)–C(1*)–C(4*)	112.2(11)	
C(2*)–H(2B*)	0.97			111.2(AV)	
C(2*)–H(2C*)	0.94		C(2)–C(1)–C(3)	111.2(12)	114.1(18)
C(3*)–H(3A*)	1.32		C(2*)–C(1*)–C(3*)	111.0(11)	
C(3*)–H(3B*)	0.86(MIN)			111.1(AV)	
C(3*)–H(3C*)	1.16		C(3)–C(1)–C(4)	105.7(12)	107.0(14)
C(4*)–H(4A*)	0.89		C(3*)–C(1*)–C(4*)	110.6(11)	
C(4*)–H(4B*)	1.18			108.2(AV)	
C(4*)–H(4C*)	0.96		C(4)–C(1)–C(2)	111.3(11)	108.7(15)
	1.05(AV)		C(4*)–C(1*)–C(2*)	108.8(12)	
				110.1(AV)	
N(1)...N(2)	2.69(1)	2.69(2)	C(2)–C(3)–C(4)	59.9(6)	60.2(7)
N(1*)...N(2*)	2.69(2)		C(2*)–C(3*)–C(4*)	60.4(5)	
	2.69(AV)			60.2(AV)	
N(1)...N(1*)	3.83(2)		C(3)–C(4)–C(2)	61.0(6)	61.0(8)
N(1)...N(1')		3.76(2)	C(3*)–C(4*)–C(2*)	59.7(5)	
N(1)...N(2*)	3.22(2)			60.4(AV)	
N(2)...N(1*)	3.29(2)		C(4)–C(2)–C(3)	59.1(7)	58.8(7)
	3.26(AV)		C(4*)–C(2*)–C(3*)	59.9(5)	
N(1)...N(2)		3.20(2)		59.9(AV)	
N(2)...N(2*)	3.66(2)				
N(2)...N(2)		3.70(3)			
C(2)...C(3)	2.54(2)	2.54(3)			
C(2*)...C(3*)	2.52(2)				
	2.53(AV)				
C(3)...C(4)	2.49(2)	2.48(2)			
C(3*)...C(4*)	2.53(2)				
	2.51(AV)				
C(4)...C(2)	2.51(2)	2.52(3)			
C(4*)...C(2*)	2.54(2)				
	2.53(AV)				

[a] For the triclinic modification, the values are arranged into sets according to a pseudo-twofold axis (which relates nonstarred and starred atoms in pairs) passing through Cu and the midpoint of N(1) and N(1*) [or N(2) and N(2*)]. For the tetragonal modification, primes refer to atoms related to those in asymmetric unit by the crystallographic twofold axis.

After successive least-squares refinements and Fourier syntheses with the 495 reflections (*i.e.*, the independent 504 minus the above-mentioned nine 0kl), all 11 nonhydrogen light atoms were located. The isotropic refinement of the derived structure with the observed, independent 504 reflections was then carried out, and an unweighted reliability index of 0.096 was obtained. A difference Fourier synthesis at this stage showed considerable anisotropic thermal motion around the copper atom. Excluding the immediate vicinity of the copper atom, the remaining positive peaks ranged from 0.3 to 0.5 e/Å^3, which may be compared with a peak-height range of 5.0–6.4 e/Å^3 [except 3.2 e/Å^3 for C(2)] observed for carbon atoms on a Fourier map based on the same atomic parameters. On the basis of stereochemical considerations together with the fact that the determined molecular geometry of the triclinic modification is similar to that of the

TABLE III
ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS (Å) ALONG THE DIRECTIONS OF THE PRINCIPAL AXES

ATOM	MIN		MED		MAX	
	TRICLINIC	TETRAGONAL	TRICLINIC	TETRAGONAL	TRICLINIC	TETRAGONAL
CU	0.206(3)	0.140(9)	0.223(4)	0.206(7)	0.251(2)	0.232(5)
N(1)	0.194(19)	0.123(47)	0.233(22)	0.216(22)	0.267(15)	0.299(20)
N(1*)	0.170(27)		0.218(12)		0.288(21)	
N(2)	0.180(19)	0.092(53)	0.254(15)	0.244(27)	0.286(16)	0.309(22)
N(2*)	0.181(22)		0.241(17)		0.314(23)	
C(1)	0.164(22)	0.089(91)	0.252(22)	0.273(29)	0.385(22)	0.310(23)
C(1*)	0.194(26)		0.263(19)		0.317(22)	
C(2)	0.175(31)	0.200(46)	0.347(17)	0.257(39)	0.403(23)	0.456(24)
C(2*)	0.259(20)		0.326(22)		0.349(16)	
C(3)	0.223(28)	0.132(42)	0.292(16)	0.236(31)	0.433(21)	0.271(23)
C(3*)	0.217(19)		0.291(19)		0.323(18)	
C(4)	0.225(16)	0.182(39)	0.311(21)	0.243(31)	0.339(17)	0.320(23)
C(4*)	0.278(22)		0.286(22)		0.348(17)	
C(5)	0.178(35)	0.094(72)	0.262(17)	0.240(32)	0.319(23)	0.369(26)
C(5*)	0.174(31)		0.230(28)		0.272(16)	
C(6)	0.202(22)	0.073(71)	0.235(25)	0.211(41)	0.302(21)	0.316(27)
C(6*)	0.199(29)		0.221(25)		0.329(28)	
C(7)	0.245(24)	0.196(39)	0.250(28)	0.232(40)	0.372(19)	0.335(28)
C(7*)	0.218(29)		0.236(17)		0.379(29)	
C(8)	0.178(29)	0.133(72)	0.279(26)	0.263(31)	0.374(18)	0.359(27)
C(8*)	0.221(28)		0.255(20)		0.355(26)	
C(9)	0.192(22)	0.127(57)	0.277(25)	0.252(31)	0.347(18)	0.312(25)
C(9*)	0.126(43)		0.306(17)		0.325(25)	

tetragonal modification, all 13 independent hydrogen atoms were identified from this map.

Without including hydrogen atoms, the refinement of the structure in which anisotropic thermal parameters were assigned only to the copper atom[33-35] resulted in R_F and R_{wF} values of 0.092 and 0.093, respectively. An attempt to carry out anisotropic refinement for all 12 nonhydrogen atoms, however, resulted in a nonpositive definite form for the temperature coefficients for C(1). With the inclusion of all 13 fixed hydrogen atoms (for which fixed isotropic temperature factors of 8.0 and 10.0 Å^2 were assigned to each of the ring and methyl hydrogens, respectively), the anisotropic refinement proceeded smoothly. After six cycles, the values of R_F and R_{wF} remained at 0.083 and 0.070, respectively. Parameter shifts in the last cycle were all less than 3% of the corresponding standard deviations. The standard deviation of an observation of unit weight was 1.64.

The final parameters with estimated standard deviations, obtained from the last cycles of the refinements, for both triclinic and tetragonal modifications, are given in Table I. Observed and calculated structure amplitudes are available to the interested reader.[36] Interatomic distances and intramolecular angles were calculated with the Busing–Martin–Levy program[37] and some selected values are summarized in Table II. Shown in Table III are root-mean-square thermal displacements along the directions of the principal axes for the nonhydrogen atoms. "Best" planes formed by sets of specified atoms and the perpendicular distances of these and other atoms from these planes were calculated by the Smith program.[38] Figures were prepared by the use of the Johnson program.[39]

Description of the Structures

The structure of each modification of $(C_9H_{13}N_2)_2Cu^{II}$ consists of discrete molecules in which each copper atom is bonded in a bidentate manner to two ligand groups. A view of the molecule along the pseudo-

(33) According to the Levy rules,[34] anisotropic thermal coefficients β_{ij} associated with the chosen symmetry-related basic copper atom (y is related to x by $y = 1 - x^{32}$) are required to possess the relations $\beta_{11} = \beta_{22}$ and $\beta_{13} = \beta_{23}$. These symmetry relations are different from those[35] of $\beta_{11} = \beta_{22}$ and $\beta_{13} = -\beta_{23}$ when the coordinates of the basic copper atom chosen are such that $y = x$.[18a]

(34) H. A. Levy, *Acta Crystallogr.*, **9**, 679 (1956).

(35) W. J. A. M. Peterse and J. H. Palm, *ibid.*, **20**, 147 (1966).

(36) A listing of structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-2315. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(37) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

(38) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, Wis., 1962.

(39) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, 2nd revision, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970.
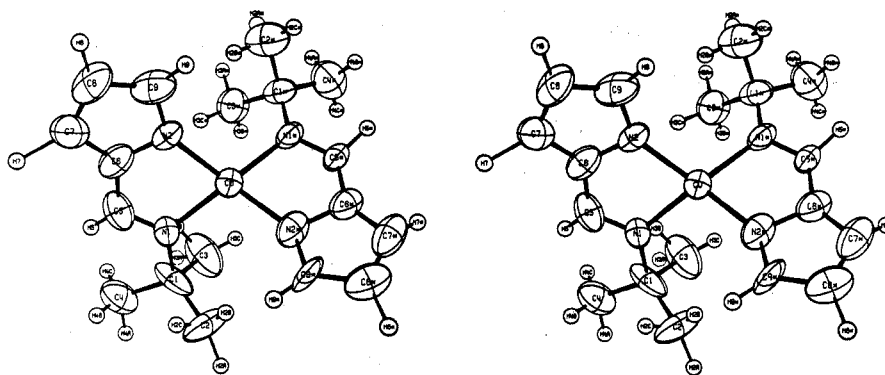
Figure 1.—Stereoscopic view of the molecular configuration for the triclinic modification along the pseudo-twofold axis passing through Cu and the midpoint of N(1) and N(1*) [or N(2) and N(2*)]. Starred atoms are related in pairs to those of the corresponding nonstarred atoms by the pseudo-twofold axis. In this figure, as well as in Figure 2, nonhydrogen atoms are shown as 50% probability thermal ellipsoids.
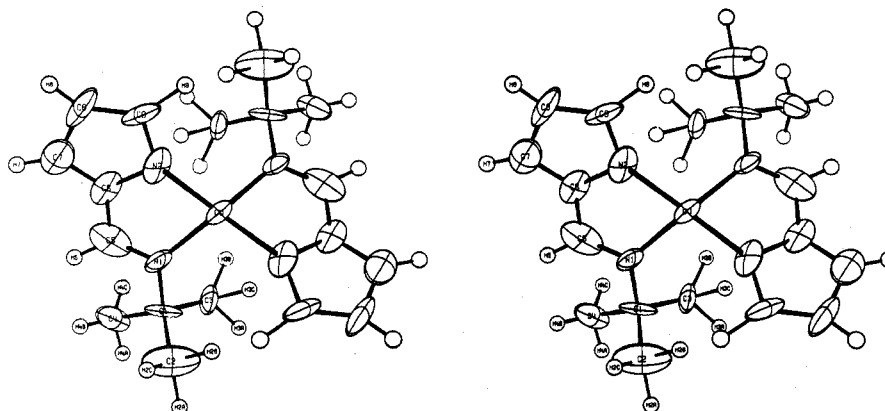

Figure 2.—Stereoscopic view of the molecular configuration for the tetragonal modification along a crystallographic twofold axis passing through Cu.

TABLE IV

VARIATIONS OF THE Cu–N DISTANCE (Å) AND THE DIHEDRAL ANGLE (DEG) BETWEEN THE COORDINATION PLANES IN SOME RELATED FOUR-COORDINATED COPPER(II) CHELATES

Chelating ligand	Coordination group	Cu–N distance	Dihedral angle	Ref
Salicylaldimine	N_2O_2	1.904	0	5
N-Methylsalicylaldimine (α form)	N_2O_2	1.99	0	42
N-Ethylsalicylaldimine (monoclinic form)	N_2O_2	1.966 (9), 1.918 (9)	35.6	7a
N-Ethylsalicylaldimine (orthorhombic form)	N_2O_2	2.005 (9), 2.000 (9)	7.4, 11.4	7b
N-n-Propylsalicylaldimine	N_2O_2	1.99 (2)	0	8
N-Isopropylsalicylaldimine	N_2O_2	1.979 (10), 1.990 (8)	59.7	9
N-n-Butylsalicylaldimine	N_2O_2	2.019 (7)	0	10
N-tert-Butylsalicylaldimine	N_2O_2	2.010 (6), 1.960 (6)	53.6	11
N-Phenylsalicylaldimine	N_2O_2	1.993 (4)	0	43
N,N'-(2,2'-Biphenyl)bis(salicylaldimine)	N_2O_2	1.96 (1), 1.94 (1)	37	44
Biurea	N_4	1.93 (av)	0	45
Dipyrromethene	N_4	1.99 (2) (av)	68	41
2,2-Bipyridylamine	N_4	1.99 (1), 1.94 (1)	55.6	14
H-Pyrrole-2-carbaldimine	N_4	1.972 (9), 1.950 (8)	0	46
N-tert-Butylpyrrole-2-carbaldimine (triclinic form)	N_4	2.054 (8) (av), 1.939 (8) (av)	61.3 (4)	Present work
N-tert-Butylpyrrole-2-carbaldimine (tetragonal form)	N_4	2.044 (14), 1.922 (15)	60.1 (9)	Present work

molecular twofold axis is shown in Figure 1 for the triclinic form, and a view along a diagonal crystallographic twofold axis is shown in Figure 2 for the tetragonal form. The overall similarity in the molecular configurations of the nonhydrogen frameworks in the two forms is apparent. Although the arrangement of the hydrogen atoms in the two molecules is not exactly the same, they are in general at the expected places, except that in the triclinic form H(3a) is not at the expected staggered position relative to N(1) when viewed down the C(1)→C(3) direction. The

average C–H bond distances in both modifications are reasonable, and no particularly unusual bond angles involving hydrogen were found.

As expected from the observed magnetic and spectral properties, which show a definite dissimilarity from those of planar or essentially planar structures for the isopropyl and n-butyl analogs,[15] the coordination around the present copper complex is that of a distorted tetrahedron for both modifications. As suggested and commonly adopted by several authors, the dihedral angle between the planes each containing

the CuN$_2$ (or CuNO) has been used as a measure of deviation from regularity of the coordination tetrahedron.[40] For the presently known four-coordinated Cu(II) complexes, this value usually occurs in the range of approximately 60° or less [except for one value at 68°[41]]. For the triclinic and tetragonal forms, the calculated values of 61.3 (4) and 60.1 (9)°, respectively (which agree with each other within two standard deviations), fall at the high end of this range. For the purpose of comparison, the various degrees of flattening of tetrahedra found for other related four-coordinated Cu(II) chelates[5,7-11,41-46] (the salicylaldimine series in particular) whose structures have been elucidated by X-ray analyses are given in Table IV. It can be seen that ligand stereochemistry strongly influences the nature of the CuN$_2$O$_2$ or CuN$_4$ coordination sphere, which ranges from planar to various degrees of distorted tetrahedral; the introduction of a bulky substituent at the pyrrole nitrogen atom can markedly disrupt the planar conformation which would otherwise be expected, as in the case of the unsubstituted bis(H-pyrrole-2-carbaldimino)copper(II).[46]

As in analogous cobalt(II)[16a] and nickel(II)[16b] complexes, the Cu–N(1) distances [weighted average value 2.054 (8) Å for the triclinic form and 2.044 (14) Å for the tetragonal form] are in each case longer by ~0.1 Å than the corresponding Cu–N(2) distances [1.939 (8) and 1.922 (15) Å for the triclinic and tetragonal, respectively]. The pertinent structural parameters for the MN$_4$ tetrahedra for (C$_9$H$_{13}$N$_2$)$_2$M^{II} where M = Co, Ni, and Cu are given in Table V. Despite the fact

TABLE V
COMPARISON OF PRINCIPAL STRUCTURAL
PARAMETERS OF(C$_9$H$_{13}$N$_2$)$_2$M^{II}

	Co	Ni	Cu Triclinic	Cu Tetragonal
		Distance, Å		
M–N(1)	2.066 (8)	2.032 (4)	2.054 (8)^a	2.044 (14)
M–N(2)	1.981 (7)	1.935 (5)	1.939 (8)^a	1.922 (15)
N(1)···N(2)	2.70 (1)	2.65 (1)	2.69 (1)^a	2.69 (1)
		Angle, deg		
N(1)–M–N(2)	83.5 (3)	83.7 (4)	84.7 (4)^a	85.4 (6)
N(1)–M–N(1') (θ_1)	121.8 (4)	116.7 (2)	137.7 (4)	133.4 (9)
N(1)–M–N(2') (θ_2)	123.5 (3)	122.1 (2)	109.2 (4)^a	107.3 (6)
N(2)–M–N(2') (θ_3)	126.2 (5)	132.7 (3)	142.1 (5)	148.1 (9)
$\|\theta_1 - \theta_2\|$	1.7 (5)	5.4 (3)	28.5 (6)	26.1 (11)
$\|\theta_3 - \theta_2\|$	2.7 (6)	10.6 (4)	31.9 (6)	40.8 (11)
b	89.6 (4)	88.7 (3)	61.3 (4)	60.1 (9)

^{a} Weighted average values. ^{b} Dihedral angle between two coordination planes each defined by the MN$_2$ moiety.

that the degree of distortion from regularity of the coordination tetrahedron increases on changing the transition metals from Co to Ni to Cu, the "bite" distances N(1)···N(2) as well as bite angles N(1)–M–N(2) are nearly invariant. Furthermore, there

(40) *E.g.*, R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, **22**, 780 (1967).
(41) M. Elder and B. R. Penfold, *J. Chem. Soc. A*, 2556 (1969).
(42) E. C. Lingafelter, G. L. Simons, B. Morosin, C. Sheringer, and C. Freiburg, *Acta Crystallogr.*, **14**, 1222 (1961).
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(44) T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 1396 (1966).
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(46) R. Tewari and R. C. Srivastava, *Acta Crystallogr., Sect. B*, **27**, 1644 (1971).
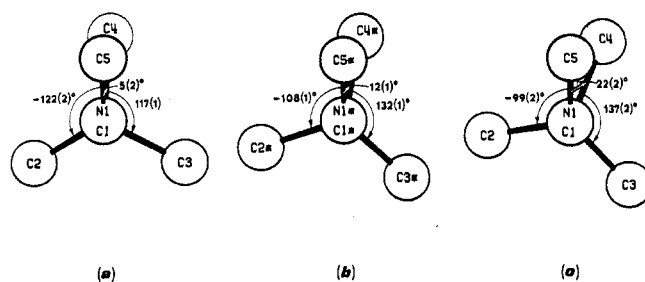
Figure 3.—Views down the N(1)→C(1) or N(1*)→C(1*) directions showing the conformations of the *tert*-butyl groups in the triclinic [(a) and (b)] and the tetragonal [(c)] modifications. In each case, three methyl carbons are in nearly eclipsed positions relative to C(5) or C(5*).

seems no systematic trend in the structural parameters of chelate pyrrole-2-carbaldimine groups as the metal is varied. The results also illustrate how a decrease in the dihedral angle between coordination planes is accompanied by an increase in the difference between bond angles N(1)–M–N(1') and N(1)–M–N(2') [or N(2)–M–N(2') and N(2)–M–N(1')], which would be 180 and 96°, respectively, if the structure were planar and if the intrachelate angle N(1)–M–N(2) were taken as 84°.

Since Cu–N(1) distances of the triclinic and tetragonal forms are longer than any other Cu–N distances listed for the other related complexes shown in Table IV, they suggest a higher limit for the bond length between copper and substituent nitrogen in the four-coordinated copper complexes. It is to be noted that in a planar structure of bis(H-pyrrole-2-carbaldimino)-copper(II)[46] the two chemically dissimilar Cu–N bond lengths are not much different [1.972 (9) and 1.950 (8) Å]. The significant difference of ~0.1 Å between M–N(1) and M–N(2) distances in the series of (C$_9$H$_{13}$-N$_2$)$_2$M^{II} complexes appears to support the previous suggestion[41] that the Cu–N(pyrrole) bond is affected by steric interference between the nitrogen substituent and the opposite ligand. However, the substitution of R groups in the present structures for hydrogen does not seem to affect the corresponding Cu–N(azomethine) distances as markedly, as shown by the comparison of 1.939 (8) and 1.92 (2) Å for the triclinic and tetragonal forms, respectively, with 1.950 (8) Å for bis(H-pyrrole-2-carbaldimino)copper(II).

One of the most interesting structural features of the copper complex is that the three methyl carbons viewed down the N(1)→C(1) bond are in near-eclipsed positions relative to C(5) as shown in Figure 3, in sharp contrast to the cobalt and nickel analogs in which they are in near-staggered positions. The existence of these different configurations of the methyl groups for the different metal atoms can be considered to arise from the fact that the steric interaction can be alleviated by a rotation of the methyl groups about the N(1)–C(1) bond, as well as a torsional motion about the axis bisecting the chelate rings, resulting in different degrees of flattening of the coordination tetrahedron. It is clear that in the present copper(II) complex, the shifting of the three methyl carbons from stable near-staggered positions for the tetrahedral or pseudotetrahedral structures to near-eclipsed positions is required to minimize the steric hindrance between N(2*) [or N(2')] and C(3) as half of the molecule including Cu,
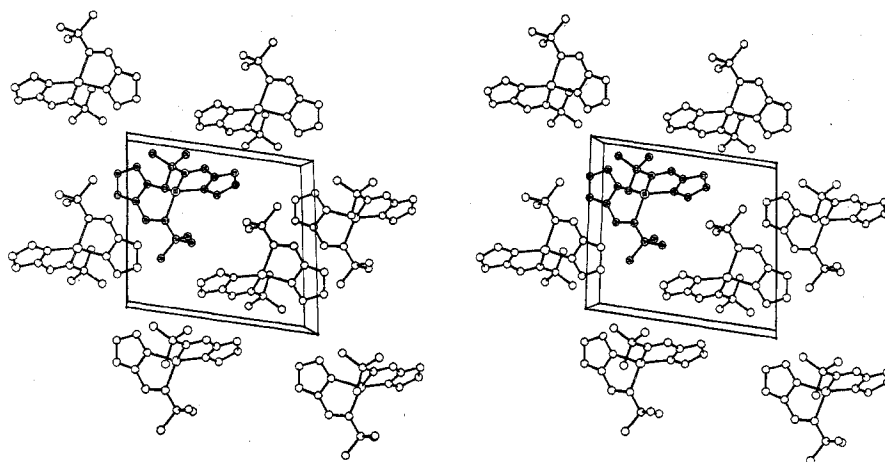
Figure 4.—Stereoscopic view down the *a* axis of the unit cell for the triclinic modification. In this figure, as well as in Figure 5, the axial systems are right handed. For the sake of clarity, hydrogen atoms are not included. The origin of the unit cell is in the upper left rear corner. Only the reference molecule is labeled.
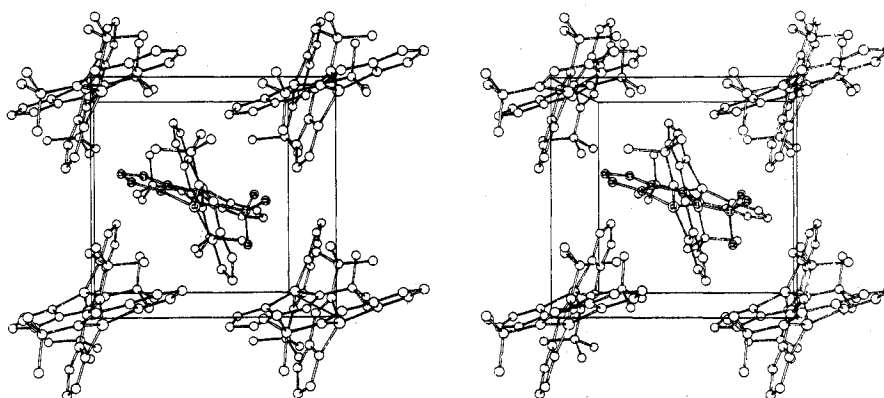

Figure 5.—Stereoscopic view down the *c* axis of the unit cell for the tetragonal modification. The origin of the unit cell is in the upper left rear corner. Only the reference atoms in the asymmetric unit are identified. At each of four corners, as well as at the center of the unit cell, two molecules are seen to be related by a crystallographic twofold screw axis along the view direction.

N(1*) [or N(1′)], and N(2*) [or N(2′)] is rotated relative to the other half of the molecule about the axis bisecting the chelate rings.

The equations of least-squares planes and perpendicular distances of atoms from these planes are listed in Table VI. A difference in structure of the triclinic form and the tetragonal form is that the copper atom is significantly out of the planes of the pyrrole–C–

TABLE VI
EQUATIONS OF LEAST-SQUARES PLANES AND DISTANCES (Å)
OF CONSTITUENT ATOMS FROM THESE PLANES[a]

(a) $-0.233X - 0.919Y - 0.318Z = 6.347$
(b) $0.871X + 0.271Y - 0.411Z = 2.851$
(c) $0.928X - 0.296Y - 0.226Z = 0.939$

	Triclinic			Tetragonal
	(a)		(b)	(c)
Cu[b]	0.175	Cu[b]	−0.124	Cu[b]	0.031
N(1)	0.05	N(1*)	−0.06	N(1)	0.02
N(2)	−0.02	N(2*)	0.07	N(2)	0.01
C(1)	−0.01	C(1*)	−0.02	C(1)	−0.01
C(5)	−0.06	C(5*)	0.09	C(5)	0.00
C(6)	−0.05	C(6*)	0.06	C(6)	−0.06
C(7)	0.04	C(7*)	−0.02	C(7)	0.04
C(8)	0.05	C(8*)	−0.09	C(8)	0.01
C(9)	−0.01	C(9*)	−0.04	C(9)	−0.01

[a] The coordinates X, Y, and Z (in Å) refer to a cartesian system with unit vectors i along b × c*, j along b, and k along c*. The weighting factor, w_k, given to each atom k forming the plane was $w_k = [a\sigma(x_k)b\sigma(y_k)c\sigma(z_k)]^{-2/3}$, where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations in fractional coordinates of the atomic coordinates x_k, y_k, and z_k, respectively.[38] [b] Atom not included in the calculation of the least-squares plane.

N–C moieties by 0.175 and 0.124 Å in the former, a phenomenon similar to that observed for bis(N-isopropylsalicylaldiminato)nickel(II),[9] while it is 0.031 Å in the latter. This structural difference is difficult to rationalize other than that it is due, at least in part, to the influence of different crystal packing.

Figure 4 gives a stereoscopic view along the *a* axis of the relative orientation of the molecules in the triclinic unit cell. Another stereoscopic view along the *c* axis for the tetragonal unit cell is shown in Figure 5. There are no abnormally short intermolecular contacts in either the triclinic or the tetragonal crystal, indicating that no unusual forces are involved in the crystal packing. The shortest nonbonding intramolecular H···H distance [excluding those for H(methyl)···H-(methyl)] is 1.88 Å for H(5*)···H(4b*) in the triclinic and 1.89 Å for H(9)···H(2b) in the tetragonal modification.

The closest intermolecular H···H contacts are 2.17 Å for H(7)···H(4a) and 1.99 Å for H(7)···H(3b) in the triclinic and tetragonal crystals, respectively.