The Molecular and Crystal Structure of the Green Form of Bis(*N*-cyclohexylsalicylideneaminato)copper(II)

Hatsue TAMURA, Kazuhide OGAWA,* Akira TAKEUCHI, and Shoichiro YAMADA
College of General Education, Osaka University, Toyonaka, Osaka 560
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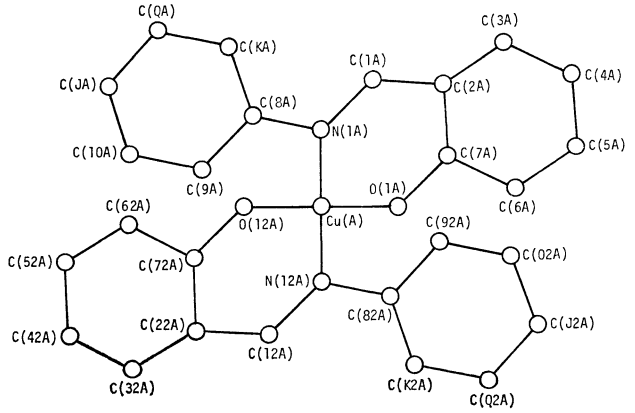
Bis(*N*-cyclohexylsalicylideneaminato)copper(II) crystallizes in two forms: one is a brown crystal (Form I), and the other is a green one (Form II). The crystal structure of Form II has been determined by X-ray analysis. The green crystals are monoclinic; space group, $P2_1/n$. The cell dimensions are $a=23.134(6)$, $b=9.525(3)$, $c=21.472(8)$ Å, $\beta=99.42(1)°$, and $Z=8$. The structure was deduced by the heavy-atom method and was refined to a final R value of 0.082 for 1883 observed reflections by the block-diagonal least-squares method. The molecular structure in Form II is dimeric, in contrast with the case of Form I, which is composed of a monomeric molecule. The two monomeric halves are joined by two Cu–O bonds with distances of 2.60(1) and 2.64(1) Å. Each copper(II) ion is penta-coordinated in a distorted square-pyramidal configuration. The molecular structures in Form I and II have been compared with those of the related Cu(II) compounds.

Among the crystal structures of various kinds of copper(II) complexes with *N*-substituted derivatives of salicylideneaminates (abbreviated as Cu(*N*-R, salim)$_2$ hereafter) so far determined, the following derivatives have been reported to have polymorphic crystals: the polymorphs of α-[1] and γ-forms[2] of bis(*N*-methylsalicylideneaminato)copper(II) (Cu(*N*-Me, salim)$_2$) have a relation of the monomer and the dimer, while the polymorphism of bis(*N*-ethylsalicylideneaminato)-copper(II), which has monoclinic[3] and orthorhombic forms,[4] is due to the different coordination geometry. It seems to be significant to examine related copper(II) complexes with isopropyl and cyclohexyl groups, which are bulkier than methyl and ethyl groups.

Two of the present authors (A.T. and S.Y.) previously synthesized the green(low-temperature form) and the brown(high-temperature form) complexes of bis(*N*-isopropyl-3-methoxysalicylideneaminato)copper(II) (Cu(*N*-*i*-Pr, 3-CH_3O-salim)$_2$) and reported their structures on the basis of the absorption spectra, thermal, and X-ray data.[5] Recently two modifications of bis(*N*-cyclohexylsalicylideneaminato)copper(II) (Cu(*N*-Ch, salim)$_2$) were also obtained by the two authors (A.T. and S.Y.); one is brown, and the other, green. Hereafter, the former and the latter will be designated as Form I and Form II respectively. With a rise in the temperature, the brown crystal melts at 165—166 °C and crystallizes in the green Form II, which melts at 176—177 °C. Crystals of Form II are also obtained by the slow evaporation of a chloroform solution of Form I. The crystals of Form II obtained by this method gave the same X-ray diffraction pattern as that of crystal obtained by heating crystals of Form I on an oil-bath at 170—180 °C. The crystal structure of Form I was reported previously.[6] In the present work, the crystal structure of Form II has been determined and compared with that of Form I.



Atom numbering scheme of the one half ([Cu(A)]) of the dimer. The same atom numbering as [Cu(A)] was used for [Cu(B)], and the distinction between the atoms in [Cu(A)] and those in [Cu(B)] was made by the letters A and B.

Experimental

The green crystals of Cu(*N*-Ch, salim)$_2$ were obtained by the slow evaporation of a chloroform solution of Form I at a temperature below 10 °C. The crystal and experimental data of Form II are listed in Table 1 and compared with those of Form I. The X-ray intensity data were measured on a Rigaku-Denki four-circle diffractometer with Zr-filtered

Table 1. Crystal and experimental data

	Form II	Form I
Color	green	brown
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a	23.134(6) Å	12.035(5) Å
b	9.525(3) Å	7.810(3) Å
c	21.472(8) Å	6.475(3) Å
α		104.86(1)°
β	99.42(1)°	102.06(1)°
γ		97.67(1)°
V	4668(2) Å^3	563.9(4) Å^3
Z	8	1
D_m	1.33 g cm^{-3}	1.37 g cm^{-3}
D_x	1.336 g cm^{-3}	1.379 g cm^{-3}
μ	10.0 cm^{-1} (for Mo $K\alpha$)	11.5 cm^{-1} (for Cu $K\alpha$)
Scan method	θ-2θ[a]	θ-2θ
Scan speed	4°min^{-1}	2°min^{-1}
Scan width	$1.2°+0.4°\tan\theta$	$1.5°+0.15°\tan\theta$
Background	2×5 s	2×10 s
$2\theta_{max}$	45° (Mo $K\alpha$)	115° (Cu $K\alpha$)

a) For weak reflections with $|F_o|<3\sigma(F_o)$, the peak scan was repeated four times.

TABLE 2. FINAL ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS, WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
Cu(A)	4854(1)	1674(2)	7555(1)	a)	Cu(B)	5203(1)	5115(2)	7495(1)	a)
O(1A)	4191(5)	1259(12)	7950(5)	4.1(3)	O(1B)	6017(4)	5442(12)	7583(5)	4.3(3)
N(1A)	5408(5)	1436(14)	8388(6)	3.6(3)	N(1B)	5202(6)	5553(15)	8417(7)	4.6(3)
C(1A)	5240(7)	1377(19)	8928(8)	4.0(4)	C(1B)	5659(8)	5751(21)	8841(9)	5.0(5)
C(2A)	4632(7)	1401(19)	9045(8)	4.2(4)	C(2B)	6261(7)	5639(19)	8701(8)	3.9(4)
C(3A)	4552(8)	1400(20)	9679(8)	4.5(4)	C(3B)	6728(8)	5770(22)	9232(9)	5.6(5)
C(4A)	3984(8)	1486(21)	9813(9)	5.2(5)	C(4B)	7298(8)	5722(21)	9145(9)	5.0(5)
C(5A)	3500(8)	1454(20)	9315(8)	4.6(4)	C(5B)	7440(7)	5585(19)	8550(8)	4.4(4)
C(6A)	3559(8)	1388(20)	8684(9)	5.0(5)	C(6B)	7014(7)	5493(19)	8005(8)	4.0(4)
C(7A)	4150(8)	1332(19)	8541(9)	4.6(4)	C(7B)	6412(7)	5514(18)	8089(8)	3.9(4)
C(8A)	6060(7)	1348(19)	8362(8)	3.9(4)	C(8B)	4606(8)	5762(21)	8622(9)	5.3(5)
C(9A)	6453(8)	1611(23)	9017(9)	6.1(5)	C(9B)	4608(10)	5578(26)	9299(8)	8.3(7)
C(10A)	7095(8)	1543(23)	8889(9)	6.2(5)	C(10B)	3948(9)	5893(24)	9396(10)	6.7(5)
C(JA)	7218(8)	93(23)	8636(9)	5.8(5)	C(JB)	3750(10)	7290(25)	9158(11)	7.8(6)
C(QA)	6811(9)	−272(24)	8011(10)	6.7(5)	C(QB)	3763(10)	7428(27)	8477(11)	8.2(6)
C(KA)	6168(8)	−152(23)	8136(9)	6.0(5)	C(KB)	4404(9)	7174(23)	8345(10)	6.4(5)
O(12A)	5477(4)	2532(12)	7204(5)	3.7(2)	O(12B)	4459(4)	4232(12)	7434(5)	4.0(2)
N(12A)	4429(5)	1151(14)	6690(6)	3.5(3)	N(12B)	5071(5)	5652(14)	6567(6)	3.1(3)
C(12A)	4645(8)	1213(19)	6171(8)	4.5(4)	C(12B)	4585(7)	5558(18)	6193(8)	3.8(4)
C(22A)	5247(7)	1738(18)	6123(7)	3.3(4)	C(22B)	4026(7)	5017(20)	6404(8)	4.0(4)
C(32A)	5409(7)	1607(19)	5534(8)	4.2(4)	C(32B)	3513(8)	5179(21)	5926(9)	5.3(5)
C(42A)	5973(7)	2101(19)	5439(8)	4.5(4)	C(42B)	2965(8)	4690(22)	6079(9)	5.8(5)
C(52A)	6344(7)	2723(18)	5958(8)	3.9(4)	C(52B)	2939(8)	4177(21)	6679(9)	5.4(5)
C(62A)	6186(7)	2854(18)	6542(8)	3.5(4)	C(62B)	3428(8)	3970(20)	7158(9)	4.9(5)
C(72A)	5619(7)	2362(18)	6644(8)	3.5(4)	C(72B)	3994(7)	4404(19)	6996(8)	4.0(4)
C(82A)	3812(7)	612(19)	6639(8)	3.9(4)	C(82B)	5576(7)	6248(18)	6318(8)	3.6(4)
C(92A)	3831(8)	−971(22)	6782(9)	5.6(5)	C(92B)	5617(7)	7816(19)	6513(8)	4.3(4)
C(02A)	3209(9)	−1481(23)	6823(10)	6.5(5)	C(02B)	6201(7)	8401(20)	6359(8)	4.5(4)
C(J2A)	2796(8)	−1167(22)	6179(9)	5.9(5)	C(J2B)	6222(7)	8214(20)	5649(8)	4.2(4)
C(Q2A)	2796(8)	390(20)	6037(9)	4.8(4)	C(Q2B)	6119(7)	6665(20)	5444(8)	4.5(4)
C(K2A)	3435(7)	898(19)	5976(8)	4.0(4)	C(K2B)	5542(7)	6091(18)	5608(8)	3.7(4)

a) Anisotropic temperature factors ($\times 10^5$) in the form of exp $[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$, with parameters:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(A)	125(6)	1269(35)	219(7)	−89(25)	48(9)	151(30)
Cu(B)	116(6)	1386(37)	239(8)	−160(25)	63(9)	−151(30)

TABLE 3(a). BOND LENGTHS (*l*/Å), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Cu(A)–O(1A)	1.91(1)	Cu(A)–O(12A)	1.92(1)	Cu(B)–O(1B)	1.89(1)	Cu(B)–O(12B)	1.90(1)
Cu(A)–N(1A)	2.04(1)	Cu(A)–N(12A)	2.02(1)	Cu(B)–N(1B)	2.02(2)	Cu(B)–N(12B)	2.03(1)
O(1A)–C(7A)	1.29(2)	O(12A)–C(72A)	1.31(2)	O(1B)–C(7B)	1.30(2)	O(12B)–C(72B)	1.32(2)
N(1A)–C(1A)	1.28(2)	N(12A)–C(12A)	1.30(2)	N(1B)–C(1B)	1.29(3)	N(12B)–C(12B)	1.27(2)
N(1A)–C(8A)	1.52(2)	N(12A)–C(82A)	1.50(2)	N(1B)–C(8B)	1.53(3)	N(12B)–C(82B)	1.48(2)
C(1A)–C(2A)	1.47(3)	C(12A)–C(22A)	1.50(3)	C(1B)–C(2B)	1.48(3)	C(12B)–C(22B)	1.53(3)
C(2A)–C(3A)	1.40(3)	C(22A)–C(32A)	1.38(3)	C(2B)–C(3B)	1.44(3)	C(22B)–C(32B)	1.44(3)
C(3A)–C(4A)	1.39(3)	C(32A)–C(42A)	1.43(3)	C(3B)–C(4B)	1.36(3)	C(32B)–C(42B)	1.44(3)
C(4A)–C(5A)	1.42(3)	C(42A)–C(52A)	1.42(3)	C(4B)–C(5B)	1.38(3)	C(42B)–C(52B)	1.39(3)
C(5A)–C(6A)	1.39(3)	C(52A)–C(62A)	1.37(2)	C(5B)–C(6B)	1.40(3)	C(52B)–C(62B)	1.41(3)
C(6A)–C(7A)	1.45(3)	C(62A)–C(72A)	1.44(2)	C(6B)–C(7B)	1.43(3)	C(62B)–C(72B)	1.47(3)
C(7A)–C(2A)	1.42(3)	C(72A)–C(22A)	1.42(2)	C(7B)–C(2B)	1.42(3)	C(72B)–C(22B)	1.41(3)
C(8A)–C(9A)	1.56(3)	C(82A)–C(92A)	1.54(3)	C(8B)–C(9B)	1.46(3)	C(82B)–C(92B)	1.55(3)
C(9A)–C(10A)	1.56(3)	C(92A)–C(02A)	1.54(3)	C(9B)–C(10B)	1.60(3)	C(92B)–C(02B)	1.55(3)
C(10A)–C(JA)	1.53(3)	C(02A)–C(J2A)	1.58(3)	C(10B)–C(JB)	1.47(3)	C(02B)–C(J2B)	1.54(3)
C(JA)–C(QA)	1.55(3)	C(J2A)–C(Q2A)	1.51(3)	C(JB)–C(QB)	1.47(3)	C(J2B)–C(Q2B)	1.55(3)
C(QA)–C(KA)	1.56(3)	C(Q2A)–C(K2A)	1.58(3)	C(QB)–C(KB)	1.57(3)	C(Q2B)–C(K2B)	1.54(3)
C(KA)–C(8A)	1.54(3)	C(K2A)–C(82A)	1.57(3)	C(KB)–C(8B)	1.51(3)	C(K2B)–C(82B)	1.52(3)
				Cu(A)–Cu(B)	3.383(3)		
				Cu(A)–O(12B)	2.60(1)		
				O(12A)–Cu(B)	2.64(1)		

TABLE 3(b). BOND ANGLES (ϕ/°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

O(1A)–Cu(A)–N(1A)	91.3(5)	N(1A)–Cu(A)–O(12A)	89.3(5)
O(1A)–Cu(A)–O(12A)	166.6(5)	N(1A)–Cu(A)–N(12A)	157.5(6)
O(1A)–Cu(A)–N(12A)	93.0(5)	O(12A)–Cu(A)–N(12A)	91.5(5)
Cu(A)–O(1A)–C(7A)	128(1)	Cu(A)–O(12A)–C(72A)	129(1)
Cu(A)–N(1A)–C(1A)	124(1)	Cu(A)–N(12A)–C(12A)	126(1)
Cu(A)–N(1A)–C(8A)	117(1)	Cu(A)–N(12A)–C(82A)	118(1)
C(1A)–N(1A)–C(8A)	119(1)	C(12A)–N(12A)–C(82A)	117(1)
N(1A)–C(1A)–C(2A)	126(2)	N(12A)–C(12A)–C(22A)	125(2)
C(1A)–C(2A)–C(7A)	122(2)	C(12A)–C(22A)–C(72A)	122(2)
C(3A)–C(2A)–C(7A)	122(2)	C(32A)–C(22A)–C(72A)	123(2)
C(2A)–C(3A)–C(4A)	119(2)	C(22A)–C(32A)–C(42A)	119(2)
C(3A)–C(4A)–C(5A)	120(2)	C(32A)–C(42A)–C(52A)	118(2)
C(4A)–C(5A)–C(6A)	123(2)	C(42A)–C(52A)–C(62A)	123(2)
C(5A)–C(6A)–C(7A)	117(2)	C(52A)–C(62A)–C(72A)	120(2)
O(1A)–C(7A)–C(2A)	125(2)	O(12A)–C(72A)–C(22A)	124(2)
C(2A)–C(7A)–C(6A)	119(2)	C(22A)–C(72A)–C(62A)	118(2)
N(1A)–C(8A)–C(9A)	113(1)	N(12A)–C(82A)–C(92A)	109(1)
N(1A)–C(8A)–C(KA)	106(1)	N(12A)–C(82A)–C(K2A)	113(1)
C(9A)–C(8A)–C(KA)	109(2)	C(92A)–C(82A)–C(K2A)	110(2)
C(8A)–C(9A)–C(10A)	105(2)	C(82A)–C(92A)–C(02A)	109(2)
C(9A)–C(10A)–C(JA)	110(2)	C(92A)–C(02A)–C(J2A)	109(2)
C(10A)–C(JA)–C(QA)	113(2)	C(02A)–C(J2A)–C(Q2A)	110(2)
C(JA)–C(QA)–C(KA)	107(2)	C(J2A)–C(Q2A)–C(K2A)	110(2)
C(8A)–C(KA)–C(QA)	109(2)	C(82A)–C(K2A)–C(Q2A)	105(1)
O(1B)–Cu(B)–N(1B)	91.7(6)	N(1B)–Cu(B)–O(12B)	90.7(6)
O(1B)–Cu(B)–O(12B)	163.2(5)	N(1B)–Cu(B)–N(12B)	152.1(6)
O(1B)–Cu(B)–N(12B)	92.5(5)	O(12B)–Cu(B)–N(12B)	93.1(5)
Cu(B)–O(1B)–C(7B)	130(1)	Cu(B)–O(12B)–C(72B)	128(1)
Cu(B)–N(1B)–C(1B)	126(1)	Cu(B)–N(12B)–C(12B)	125(1)
Cu(B)–N(1B)–C(8B)	117(1)	Cu(B)–N(12B)–C(82B)	117(1)
C(1B)–N(1B)–C(8B)	117(2)	C(12B)–N(12B)–C(82B)	118(1)
N(1B)–C(1B)–C(2B)	122(2)	N(12B)–C(12B)–C(22B)	123(2)
C(1B)–C(2B)–C(7B)	125(2)	C(12B)–C(22B)–C(72B)	125(2)
C(3B)–C(2B)–C(7B)	118(2)	C(32B)–C(22B)–C(72B)	122(2)
C(2B)–C(3B)–C(4B)	120(2)	C(22B)–C(32B)–C(42B)	117(2)
C(3B)–C(4B)–C(5B)	121(2)	C(32B)–C(42B)–C(52B)	120(2)
C(4B)–C(5B)–C(6B)	123(2)	C(42B)–C(52B)–C(62B)	125(2)
C(5B)–C(6B)–C(7B)	117(2)	C(52B)–C(62B)–C(72B)	115(2)
O(1B)–C(7B)–C(2B)	122(2)	O(12B)–C(72B)–C(22B)	122(2)
C(2B)–C(7B)–C(6B)	121(2)	C(22B)–C(72B)–C(62B)	121(2)
N(1B)–C(8B)–C(9B)	114(2)	N(12B)–C(82B)–C(92B)	107(1)
N(1B)–C(8B)–C(KB)	104(2)	N(12B)–C(82B)–C(K2B)	114(1)
C(9B)–C(8B)–C(KB)	117(2)	C(92B)–C(82B)–C(K2B)	111(1)
C(8B)–C(9B)–C(10B)	105(2)	C(82B)–C(92B)–C(02B)	108(1)
C(9B)–C(10B)–C(JB)	112(2)	C(92B)–C(02B)–C(J2B)	110(2)
C(10B)–C(JB)–C(QB)	112(2)	C(02B)–C(J2B)–C(Q2B)	111(2)
C(JB)–C(QB)–C(KB)	110(2)	C(J2B)–C(Q2B)–C(K2B)	112(2)
C(8B)–C(KB)–C(QB)	108(2)	C(82B)–C(K2B)–C(Q2B)	107(1)
O(1A)–Cu(A)–O(12B)	86.8(4)	O(1B)–Cu(B)–O(12A)	84.5(4)
N(1A)–Cu(A)–O(12B)	110.6(5)	N(1B)–Cu(B)–O(12A)	117.6(5)
O(12A)–Cu(A)–O(12B)	80.5(4)	O(12B)–Cu(B)–O(12A)	79.7(4)
N(12A)–Cu(A)–O(12B)	91.7(5)	N(12B)–Cu(B)–O(12A)	90.3(5)
Cu(A)–O(12A)–Cu(B)	94.5(4)	Cu(A)–O(12B)–Cu(B)	96.2(5)

Mo $K\alpha$ radiation. Of 3231 independent reflections collected by the 2θ-θ scan technique, 1348 reflections with $|F_o|<3\sigma(|F_o|)$ were not used in the subsequent calculation. The data were corrected for Lorentz and polarization effects, but not for absorption. The crystal size was $0.15\times0.20\times0.30$ mm.

Structure Determination. The crystal structure was solved by the heavy-atom technique, and the refinement was performed by a block-diagonal least-squares calculation. The function minimized was $\sum w(F_o-|F_c|)^2$, with $w=1.0$ for all reflections. All the atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[7] The computations were carried out on a NEAC 2200-700 computer at Osaka University. The computer programs used in the calculations were RSSFR-5,[8] HBLS-V,[9] and DAPH[10]

in the UNICS. The final R value was 0.082. A list of observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7938).

Results and Discussion

Table 2 lists the final atomic and thermal parameters, along with the estimated standard deviations. The bond distances and angles are also listed in Table 3.

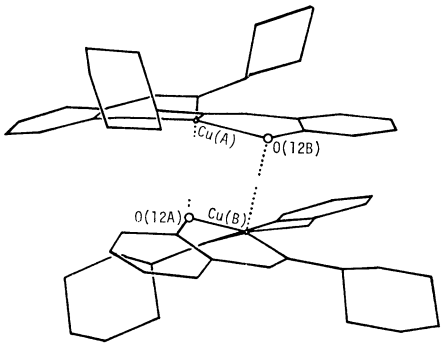


Fig. 1. Dimeric structure.

The molecular structure is shown in Fig. 1. The two crystallographically independent Cu(*N*-Ch, salim)$_2$ molecules are joined by two Cu–O bonds, with distances of 2.60 and 2.64 Å, forming a dimer. Hereafter, the two halves of the dimer will be denoted by [Cu(A)] and [Cu(B)]. Each copper(II) ion in [Cu(A)] or [Cu(B)] is penta-coordinated in a distorted square-pyramidal configuration. The basal plane of the pyramid is tetrahedrally distorted; the angle between the plane through Cu(A), O(1A), N(1A), and the plane through Cu(A), O(12A), N(12A) in [Cu(A)] is 26°, and the corresponding angle in [Cu(B)] is 32°. The coordination geometry is different from that in Form I: the Cu(II) ion in Form I has a planar coordination and the molecule is bent or stepped, so that the distance (step height) between the salicylideneamine planes is 1.28 Å. [Cu(A)] has almost the same structure as [Cu(B)]. The equations of the best planes through the three selected sets of atoms in each salicylideneamine moiety are given in Table 4(a). The displacements of the atoms from these planes and the dihedral angles between them are given in Tables 4(b) and 4(c) respectively. The dihedral angle between Plane(II) of the salicylideneamine moiety and the plane through the copper, oxygen, and nitrogen atoms ranges from 165° to 167°. (The corresponding angle in Form I is 153.5°). As may be seen in Fig. 1, the cyclohexyl groups lie outside the basal planes so as to avoid the non-bonded repulsion between the groups in one Cu(*N*-Ch, salim)$_2$ moiety and the atoms of the opposite moiety. The bond distances and angles in Form II are almost in complete agreement with those in Form I, within the limits of experimental accuracy.

The crystal structure is shown in Fig. 2. There are no

Table 4(a). Equations of best planes
$lX+mY+nZ=p$[a]

Plane	l	m	n	p
[Cu(A)]				
IA	0.131	−0.972	−0.198	−3.595
IIA	−0.001	−1.000	0.028	−0.811
IIIA	0.031	−0.999	0.021	−0.659
Ia	−0.484	0.873	−0.058	−3.688
IIa	−0.363	0.894	−0.262	−5.555
IIIa	−0.375	0.891	−0.255	−5.571
[Cu(B)]				
IB	−0.139	0.963	−0.229	−0.252
IIB	−0.008	−0.996	0.093	−3.746
IIIB	−0.003	−0.996	0.092	−3.715
Ib	0.446	−0.867	−0.221	−3.535
IIb	0.230	−0.902	−0.366	−7.679
IIIb	0.267	−0.892	−0.365	−7.316

a) $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

Table 4(b). Displacements of atoms from best planes ($\times 10^2$ Å)

	IA	IIA	IIIA		Ia	IIa	IIIa
[Cu(A)]							
Cu(A)	0	−35[a]	−32[a]	Cu(A)	0	−33[a]	−31[a]
O(1A)	0	7	4	O(12A)	0	3	2
N(1A)	0	−7	−3	N(12A)	0	−5	−3
C(1A)		1	3	C(12A)		4	4
C(2A)		−0	−3	C(22A)		0	−1
C(3A)		4	−1[a]	C(32A)		1	−2[a]
C(4A)		−4	−13[a]	C(42A)		−0	−6[a]
C(5A)		−3	−15[a]	C(52A)		−1	−6[a]
C(6A)		−1	−10[a]	C(62A)		−1	−5[a]
C(7A)		4	−1	C(72A)		−0	−2

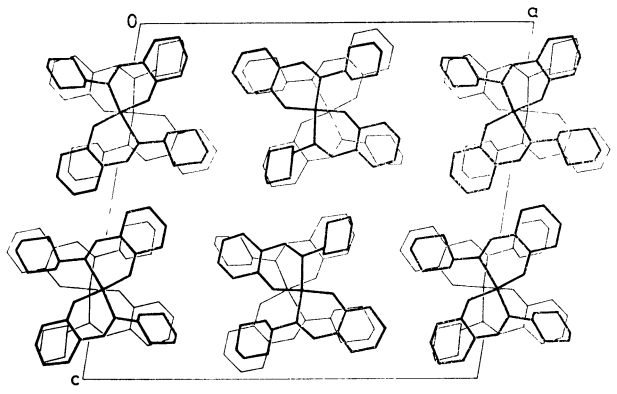
	IB	IIB	IIIB		Ib	IIb	IIIb
[Cu(B)]							
Cu(B)	0	29[a]	29[a]	Cu(B)	0	−36[a]	−31[a]
O(1B)	0	−2	−1	O(12B)	0	5	3
N(1B)	0	6	5	N(12B)	0	−10	−5
C(1B)		−5	−5	C(12B)		4	6
C(2B)		1	2	C(22B)		3	−1
C(3B)		−1	2[a]	C(32B)		3	−5[a]
C(4B)		0	2[a]	C(42B)		2	−11[a]
C(5B)		1	3[a]	C(52B)		−6	−21[a]
C(6B)		0	2[a]	C(62B)		−3	−15[a]
C(7B)		1	2	C(72B)		3	−3

a) Not included in the estimations of the equations.

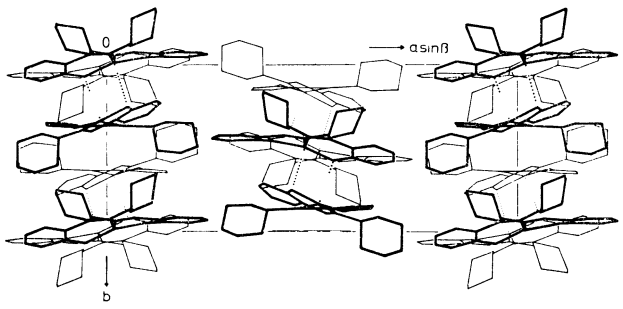
Table 4(c). Dihedral angles(°)

	IIA	IIIA	Ia	IIa	IIIa
[Cu(A)]					
IA	165	166	26		
IIA		178			
Ia				166	167
IIa					179

	IIB	IIIB	Ib	IIb	IIIb
[Cu(B)]					
IB	167	168	32		
IIB		180			
Ib				165	167
IIb					178



(a) b axis projection.



(b) c axis projection.

Fig. 2. Crystal structure.

TABLE 5. STEP-HEIGHTS IN SQUARE-PLANAR Cu(*N*-R, salim)$_2$

R	Step-height(l/Å)	Ref.
Me(α-form)	0	1
H	0.29	13
Propyl	0.32	14
Butyl	0.74	15
Phenyl	0.89	16
Ch(Form I)	1.28	6

intermolecular distances less than 3.65 Å in the crystal structure.

Most of the monomeric Cu(*N*-R, salim)$_2$-type complexes whose coordination geometry is square-planar are bent or stepped. Table 5 lists the step heights in a series of square-planar salicylideneaminato complexes. The bulkier the *N*-substituents (R) are, the larger the step heights are, except for the case of Cu(*N*-H, salim)$_2$. The large step height (1.28 Å) in Form I probably results from the interligand interaction between the bulky cyclohexyl substituent and the opposite ligand. The dimerization of the two Cu(*N*-Ch, salim)$_2$ molecules of Form I occurs by means of the formation of the Cu–O bands. Of the two ligands in a monomeric molecule, the O atom of one ligand (Type i) participates in the Cu–O bond, but that of the other ligand (Type ii) does not. In the Type i ligand the bond formation gives rise to an approach of the salicylideneamine portion to the opposite molecule, while the *N*-cyclohexane portion becomes somewhat distant from the opposite one because of the non-bonded repulsion. Consequently, the Cu$\langle^{N}_{O}$ plane of the Type i ligand slants against that of the Type ii ligand in each monomeric unit, and the disposition of the donor atoms become tetrahedral.

The dimeric molecular structure of Form II is similar to that of the γ-form of Cu(*N*-Me, salim)$_2$, but the configuration of atoms at the basal plane in Form II is much more distorted tetrahedrally than that in the γ-form of Cu(*N*-Me, salim)$_2$, because the *N*-substituents of Form II are bulkier than those of the γ-form of Cu(*N*-Me, salim)$_2$: the angle between the plane through Cu(A), O(1A), N(1A) and the plane through Cu(A), O(12A), N(12A) in [Cu(A)] is 26°, and the corresponding angle in [Cu(B)] is 32°, as has been described above; on the other hand, the corresponding angles in the γ-form of Cu(*N*-Me, salim)$_2$ are 11 and 12°.

The polymorphism in Cu(*N*-Ch, salim)$_2$ is caused by such a chemical change. On the other hand, in the case of Cu(*N*-*i*-Pr, 3-CH_3O-salim)$_2$, which has two crystal forms—the green complex (low-temperature form)[11] and the brown one(high-temperature form),[12] it has become apparent that its polymorphism is not due to dimerization, but to the difference between the coordination configurations about the Cu(II) ions(the dihedral angle between Cu, O, N planes in the low-temperature form is 47.4° and the corresponding angle in the high-temperature one is 57.9°), and also to the difference between the molecular geometry (twisted-umbrella shape in the low-temperature form and twisted-stepped shape in the high-temperature one).

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