Crystal and Molecular Structure of Bis(*N*-allylsalicylideneiminato)-nickel(II) and -Copper(II)

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The crystal and molecular structure of the title complexes have been determined by *X*-ray diffraction using visually estimated intensity data. The nickel compound has a = 13.965(10), b = 7.403(10), c = 8.912(9) Å, β = 99.3(9)°, Z = 2, and space group $P2_1/a$, while the copper compound has a = 10.871(8), b = 7.576(10), c = 27.579(7) Å, β = 127.0(8)°, Z = 4, and space group $P2_1/c$. The co-ordination plane in the nickel case is tilted by *ca.* 22° towards the salicylaldimine plane and the two salicylaldimine planes have a significant step *ca.* 1.02 Å at Ni. The salicylaldimine groups in the copper case are only slightly tilted relative to the co-ordination plane, which has a small tetrahedral distortion.

SCHIFF-BASE complexes containing different central metal atoms such as Cu, Ni, Co, and Pd have been studied in great detail for their enzymatic reactions, steric effects, and for various crystallographic features. Considerable attention has been paid to the structural changes occurring as a result of variation of the size and nature of the substituent on the N of the salicylaldimine (for brevity henceforth termed saln). In a review of bis(chelate)metal(II) complexes, Holm and O'Connor[1] suggested that complexes of four-co-ordinate Cu and Ni with N and O as donor atoms have a ***trans*** square-planar stereochemistry when the substituent on N is no larger than H, but that in the presence of large substituents the configuration is either stepped planar or pseudotetrahedral.

It is of interest to see how a small unsaturated linear-chain substituent such as an allyl group affects the molecular geometry in two molecules which differ only in the central metal atom, Cu and Ni, and whose charge and orbital energies are similar. The complex [Ni(asaln)$_2$] (asaln = *N*-allylsalicylideneiminate) is paramagnetic (*m* = 3.10 B.M.) † in pyridine solution[2] probably due to molecular association, but in the solid state it is diamagnetic[3] indicating that there may be no Ni $\cdots$ Ni intermolecular interaction. Preliminary accounts of [Cu(asaln)$_2$][4] and [Ni(asaln)$_2$][5] were reported earlier, and the structure of [Pd(asaln)$_2$][6] has also recently been determined.

EXPERIMENTAL

The complex [Ni(asaln)$_2$] was prepared by the method of Holm,[3] and purification and crystallization were carried out from acetone solution. The complex [Cu(asaln)$_2$] was synthesized by adding an alcoholic solution of allylamine to a solution of bis(salicylaldehydato)copper(II) in ethanol and refluxing the mixture for *ca.* 1 h. After several days, dark tan crystals of rhombic shape separated out. They were recrystallized from chloroform.

Crystal Data.—[Ni(asaln)$_2$], $C_{20}H_{20}N_2NiO_2$, M = 378.7, Monoclinic, a = 13.965(10), b = 7.403(10), c = 8.912(9) Å, β = 99.3(9)°, U = 909 Å^3, $F(000)$ = 396, D_m = 1.36 g cm^{-3} (flotation), Z = 2, D_c = 1.38, space group $P2_1/a$, μ(Cu-K_α) = 15.94 cm^{-1}, λ = 1.541 8 Å.

[Cu(asaln)$_2$], $C_{20}H_{20}CuN_2O_2$, M = 383.5, Monoclinic, a = 10.871(8), b = 7.576(10), c = 27.579(7) Å, β = 127.0(8)°, U = 1 814 Å^3, $F(000)$ = 796, D_m = 1.44 g cm^{-3} (flotation), Z = 4, D_c = 1.404, space group $P2_1/c$ (selected because morphologically convenient), μ(Cu-K_α) = 18.53 cm^{-1}, λ = 1.541 8 Å.

Refinement of cell parameters was carried out using the CELPAR program of Wadhavan.[7] The reciprocal-lattice levels $h0l$—$h4l$ in each case were recorded on a Stoe Weissenberg camera with nickel-filtered Cu-K_α radiation by the multiple-film technique using exposures of 100 h for each layer. The crystal of the nickel compound used for intensity-data collection had dimensions ≈ 0.50 × 0.29 × 0.20 mm, while that of the copper was ≈ 0.40 × 0.31 × 0.19 mm. Estimation of integrated intensity was done visually for 915 reflections from the nickel compound and for 2 007 reflections from the copper compound. Corrections were applied for Lorentz and polarization effects, but not for absorption or anomalous dispersion.

Structure Determination.—[Ni(asaln)$_2$]. The structure was solved by the heavy-atom method. The electron-density map[8] obtained by placing Ni at 0,0,0 gave the positions of the atoms of the chelate ring, and a series of electron-density maps revealed the positions of the remaining non-hydrogen atoms of the asymmetric unit. Least-squares refinement of the positional and isotropic parameters using the block-diagonal method[9] gave R 0.18. Further refinement involving anisotropic temperature factors for non-hydrogen atoms reduced R to 0.13. Hydrogen atoms were placed at calculated positions[10] and the B factors used were those of the C atoms to which the H atoms were attached. Finally R reduced to 0.09. In most cases the final shifts in the positional parameters were in the fifth decimal place, *i.e.* 0.01—1.0σ, except in the case of C(2) where the values were slightly more than 1.0σ.

[Cu(asaln)$_2$]. A three-dimensional Patterson synthesis[8] showed that the Cu atoms were in general positions rather than in two independent sets of special positions, and these were taken to be 0.060,0.25,0.367. The positions of all other non-hydrogen atoms were located from successive Fourier syntheses each phased by an increasing number of atoms. Full-matrix least-squares refinement[11] of their positional and anisotropic thermal parameters reduced R to 0.11, but, although the structural features of the molecules were more or less as expected, large discrepancies occurred in the values of certain bond lengths and interbond angles and some impossibly short intermolecular contacts occurred. We are indebted to a referee for pointing out that the Patterson function was ambiguous and that the

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† Throughout this paper: 1. B.M. ≈ 9.27 × 10^{-24} A m^2.

alternative Cu position 0.06,0.258 7,0.115 8 was more probable.

Starting afresh with this position in fact gave distinctly better results and removed all the discrepancies which were observed in the earlier solution. Hydrogen atoms were placed at calculated positions and each was given an isotropic B value of 5.0 Å^2. Anisotropic refinement of non-hydrogen atoms using the block-diagonal least-squares method reduced R to 0.075. In the final cycle of refinement, the shifts were mostly in the fifth decimal place, *i.e.* 0.01—1.0σ, except in the case of C(12) where they were a little more than 1.0σ. From our earlier study of the i.r. spectrum [4] in KBr the presence of one or two molecules of water was indicated, but the difference-Fourier synthesis did not show any. The atomic scattering factors used were taken from ref. 12. Observed and calculated structure factors and anisotropic thermal parameters for both structures are available as Supplementary Publication No. SUP 23083 (9 pp.).* Positional parameters of the non-hydrogen atoms are given in Tables 1 and 2, bond lengths and interbond angles in Tables 3 and 4, and deviations of selected atoms from various least-squares planes and the interplanar angles in Tables 5 and 6.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms along with their estimated standard deviations in parentheses, for $[\mathrm{Ni(asaln)_2}]$

Atom	x	y	z
Ni	5 000	5 000	0
O	4 624(6)	4 586(12)	1 860(7)
N	4 132(5)	3 228(14)	−994(8)
C(1)	3 780(8)	3 946(13)	2 070(9)
C(2)	3 509(8)	4 170(17)	3 562(9)
C(3)	2 577(8)	3 579(17)	3 854(11)
C(4)	1 933(6)	2 711(16)	2 711(9)
C(5)	2 191(7)	2 446(13)	1 339(11)
C(6)	3 078(6)	3 071(19)	945(9)
C(7)	3 356(7)	2 611(13)	−484(10)
C(8)	4 284(8)	2 353(12)	−2 461(10)
C(9)	5 177(9)	1 117(18)	−2 246(11)
C(10)	5 834(10)	0 976(28)	−3 028(10)

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms, along with their estimated standard deviations in parentheses, for $[\mathrm{Cu(asaln)_2}]$

Atom	x	y	z
Cu	609(1)	2 383(1)	6 158(0)
O(1)	−886(4)	2 195(7)	5 319(1)
O(2)	2 048(4)	2 739(6)	7 001(1)
N(1)	2 080(4)	3 392(11)	6 027(2)
N(2)	−897(4)	1 263(10)	6 277(2)
C(1)	−795(5)	2 327(9)	4 864(3)
C(2)	−1 995(7)	1 742(12)	4 269(2)
C(3)	−1 969(8)	1 928(16)	3 784(3)
C(4)	−0 652(7)	2 617(12)	3 857(3)
C(5)	539(6)	2 985(12)	4 436(3)
C(6)	520(5)	2 999(10)	4 944(2)
C(7)	1 923(4)	3 566(11)	5 537(2)
C(8)	3 708(5)	3 953(10)	6 605(3)
C(9)	4 819(5)	2 527(7)	6 939(2)
C(10)	6 123(6)	2 347(10)	6 991(3)
C(11)	2 024(6)	2 357(9)	7 461(3)
C(12)	3 387(6)	2 497(11)	8 045(3)
C(13)	3 434(7)	2 135(11)	8 572(3)
C(14)	2 162(7)	1 180(11)	8 472(3)
C(15)	924(8)	798(13)	7 900(3)
C(16)	780(6)	1 391(10)	7 365(3)
C(17)	−605(5)	926(10)	6 796(3)
C(18)	−2 496(4)	802(9)	5 706(2)
C(19)	−3 647(6)	2 332(10)	5 380(2)
C(20)	−4 887(7)	2 382(10)	5 356(3)

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\mathrm{Ni(asaln)_2}]$

Ni–O	1.844(7)	N–Ni–O	93.0(3)
Ni–N	1.905(9)	Ni–O–C(1)	125.5(7)
O–C(1)	1.311(14)	C(7)–N–C(8)	112.9(8)
N–C(7)	1.323(12)	C(7)–N–Ni	125.0(7)
N–C(8)	1.505(12)	Ni–N–C(8)	122.2(6)
C(1)–C(2)	1.450(13)	O–C(1)–C(2)	117.6(9)
C(1)–C(6)	1.438(14)	O–C(1)–C(6)	126.2(9)
C(2)–C(3)	1.436(16)	C(6)–C(1)–C(2)	116.2(9)
C(3)–C(4)	1.401(14)	C(1)–C(2)–C(3)	120.7(10)
C(4)–C(5)	1.344(13)	C(2)–C(3)–C(4)	120.2(10)
C(5)–C(6)	1.418(14)	C(3)–C(4)–C(5)	119.5(9)
C(6)–C(7)	1.431(12)	C(4)–C(5)–C(6)	123.5(9)
C(8)–C(9)	1.533(16)	C(5)–C(6)–C(1)	119.9(9)
C(9)–C(10)	1.243(17)	C(5)–C(6)–C(7)	121.1(9)
		C(1)–C(6)–C(7)	118.4(9)
Bite		C(6)–C(7)–N	125.4(9)
N · · · O	2.72	N–C(8)–C(9)	112.0(8)
		C(8)–C(9)–C(10)	129.7(11)

TABLE 4

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\mathrm{Cu(asaln)_2}]$

Cu–O(1)	1.868(3)	C(4)–C(5)	1.348(11)
Cu–O(2)	1.883(3)	C(5)–C(6)	1.413(10)
Cu–N(1)	1.993(6)	C(6)–C(7)	1.477(8)
Cu–N(2)	2.038(6)	C(8)–C(9)	1.461(9)
O(1)–C(1)	1.322(7)	C(9)–C(10)	1.344(10)
O(2)–C(11)	1.315(8)	C(11)–C(12)	1.390(10)
N(1)–C(7)	1.263(7)	C(11)–C(16)	1.416(11)
N(1)–C(8)	1.568(8)	C(12)–C(13)	1.448(10)
N(2)–C(17)	1.292(7)	C(13)–C(14)	1.433(13)
N(2)–C(18)	1.527(7)	C(14)–C(15)	1.351(10)
C(1)–C(2)	1.418(8)	C(15)–C(16)	1.459(11)
C(1)–C(6)	1.403(10)	C(16)–C(17)	1.417(9)
C(2)–C(3)	1.362(10)	C(18)–C(19)	1.537(10)
C(3)–C(4)	1.420(14)	C(19)–C(20)	1.310(11)
Bites			
N(1) · · · O(1)	2.73	N(2) · · · O(2)	2.79
O(1)–Cu–N(1)	90.0(2)	C(1)–C(6)–C(7)	123.7(6)
O(1)–Cu–N(2)	89.1(2)	C(5)–C(6)–C(7)	118.5(6)
O(2)–Cu–N(1)	90.5(2)	N(1)–C(7)–C(6)	122.6(6)
O(2)–Cu–N(2)	90.7(2)	N(1)–C(8)–C(9)	116.1(5)
Cu–O(1)–C(1)	131.6(4)	C(8)–C(9)–C(10)	124.1(5)
Cu–O(2)–C(11)	132.4(4)	O(2)–C(11)–C(12)	118.4(6)
Cu–N(1)–C(7)	128.9(5)	O(2)–C(11)–C(16)	120.3(6)
Cu–N(1)–C(8)	117.2(4)	C(12)–C(11)–C(16)	119.2(7)
C(7)–N(1)–C(8)	113.8(6)	C(11)–C(12)–C(13)	121.3(7)
Cu–N(2)–C(17)	125.2(5)	C(12)–C(13)–C(14)	117.1(7)
Cu–N(2)–C(18)	117.1(4)	C(13)–C(14)–C(15)	120.1(8)
C(17)–N(2)–C(18)	117.8(6)	C(14)–C(15)–C(16)	122.6(8)
O(1)–C(1)–C(2)	122.1(6)	C(11)–C(16)–C(15)	117.5(7)
O(1)–C(1)–C(6)	120.0(6)	C(11)–C(16)–C(17)	126.5(7)
C(2)–C(1)–C(6)	115.9(6)	C(15)–C(16)–C(17)	116.0(7)
C(1)–C(2)–C(3)	123.7(7)	N(2)–C(17)–C(16)	124.4(6)
C(2)–C(3)–C(4)	120.9(8)	N(2)–C(18)–C(19)	116.8(5)
C(3)–C(4)–C(5)	114.3(8)	C(18)–C(19)–C(20)	120.2(6)
C(4)–C(5)–C(6)	126.9(8)	O(1)–Cu–O(2)	175.6(2)
C(1)–C(6)–C(5)	117.5(6)	N(1)–Cu–N(2)	177.8(2)

DISCUSSION

$[\mathrm{Ni(asaln)_2}]$. The crystals comprise centrosymmetric molecules arranged as shown in the [001] projection in Figure 1. A thermal ellipsoid plot [13] at 50% probability of half a molecule is shown in Figure 2. The nickel-co-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

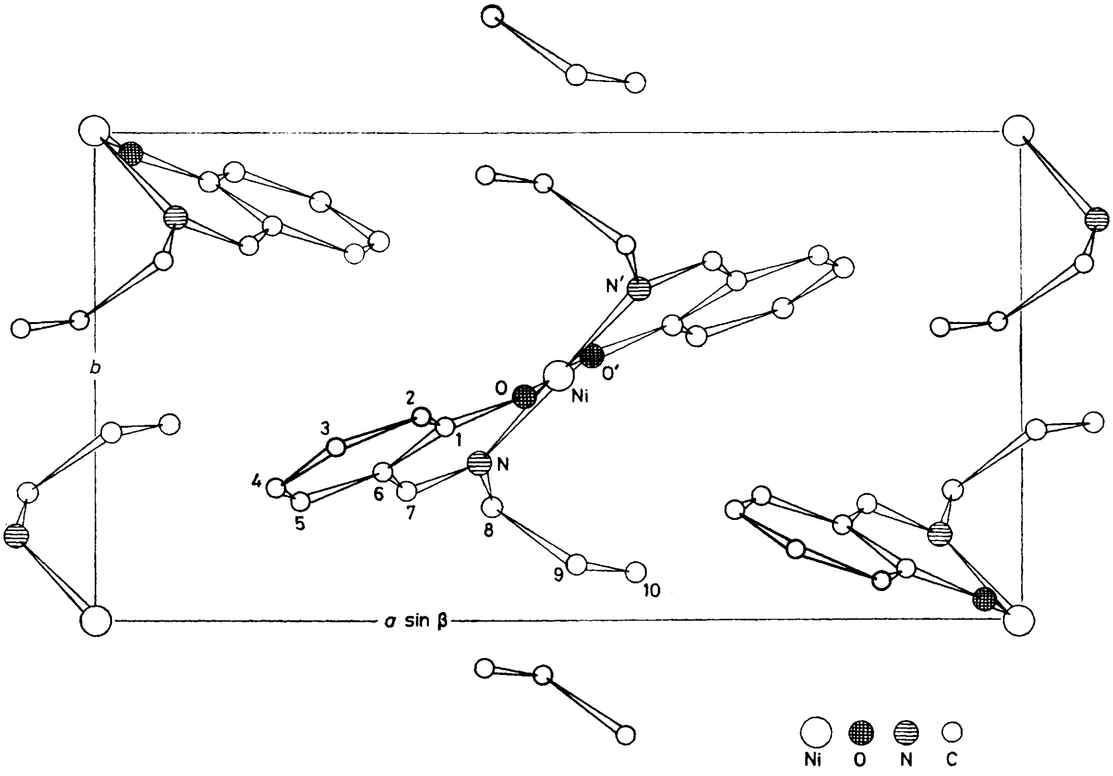

FIGURE 1 [100] Projection of the unit-cell contents of [Ni(asaln)$_2$]

ordination is accurately planar and, as shown by the data in Table 5, tilted at *ca.* 22° to the two parallel saln planes which are, therefore, stepped by *ca.* 1.02 Å. Stepped configurations have also been observed in several other nickel saln compounds (Table 7). From the magnitudes of the steps in these compounds it is clear that there is no direct relationship between the length of the linear chain substituent on salicylaldimine and the step at Ni· Obviously the large value of the step in the present molecule allows more clearance between C(8) and O', and

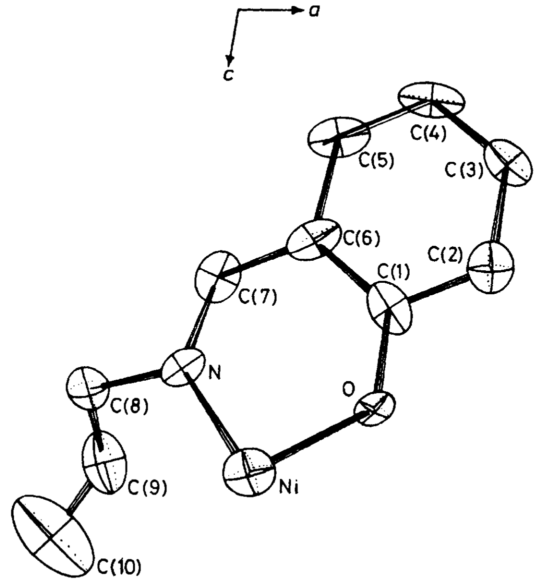

FIGURE 2 Thermal ellipsoid plot at 50% probability and the numbering scheme for half the centrosymmetric molecule of [Ni(asaln)$_2$]

TABLE 5

Least-squares planes in [Ni(asaln)$_2$] expressed in orthogonalized space as $lX + mY + nZ - p = 0$. The orthogonal axes have X along a, Y in ab plane, and Z along c^*. Deviations (Å) of atoms from the planes given in square brackets (non-defining atoms are italicized)

Plane I (Co-ordination)

$-0.6885X + 0.6962Y - 0.2032Z + 2.2302 = 0$

[Ni 0.00, O 0.00, N 0.00, *C*(7) 0.39]

Plane II (Chelate ring)

$-0.3806X + 0.8668Y - 0.3223Z - 0.0660 = 0$

[O −0.01, N 0.04, C(1) −0.02, C(6) 0.05, C(7) −0.06, *Ni* 0.48, *C*(8) −0.27]

Plane III (Benzene)

$-0.3655X + 0.8842Y - 0.2909Z - 0.2311 = 0$

[C(1) 0.00, C(2) −0.02, C(3) 0.01, C(4) 0.01, C(5) −0.02, C(6) 0.02, *Ni* 0.49, *O* 0.03, *C*(7) −0.14, *N* −0.02]

Plane IV (Saln)

$-0.3713X + 0.8749Y - 0.3111Z - 0.1393 = 0$

[C(1) 0.00, C(2) −0.04, C(3) −0.01, C(4) 0.02, C(5) 0.01, C(6) 0.05, C(7) 0.08, O 0.02, N 0.03, *Ni* 0.51, *C*(8) −0.29]

Plane V (Allyl group)

$0.4428X - 0.7033Y - 0.5562Z + 2.8271 = 0$

[C(8) 0.00, C(9) 0.00, C(10) 0.00, *Ni* −2.87, *N* −0.99]

Dihedral angles (°)

I–II	21.4	II–IV	1.0
I–III	22.1	II–V	105.2
I–IV	21.9	III–IV	1.3
I–V	94.1	III–V	107.4
II–III	2.2	IV–V	106.1

Table 6

Least-squares planes for $[Cu(asaln)_2]$

Plane I (Co-ordination)

$-0.4108X + 0.9099Y - 0.0574Z - 4.8107 = 0$

[O(1) 0.05, O(2) 0.05, N(1) −0.05, N(2) −0.05, *Cu* −0.02, *C*(7) −0.13, *C*(1) −0.15, *C*(17) −0.13, *C*(11) −0.06]

Plane II (Chelate I)

$-0.3317X + 0.9328Y - 0.1409Z - 3.1241 = 0$

[O(1) −0.03, N(1) −0.03, C(7) 0.03, C(1) −0.02, C(6) −0.00, *Cu* −0.18]

Plane III (Chelate II)

$-0.4743X + 0.8790Y + -0.0491Z - 5.5502 = 0$

[O(2) −0.03, N(2) 0.02, C(17) −0.01, C(11) 0.04, C(16) −0.02, *Cu* −0.10]

Plane IV (Allyl I)

$-0.7540X - 0.6141Y - 0.2333Z + 0.0076 = 0$

[C(8) 0.00, C(9) 0.00, C(10) 0.00, *Cu* 1.44, *N*(1) 1.28]

Plane V (Allyl II)

$0.0191X - 0.5178Y - 0.8553Z - 9.9206 = 0$

[C(18) 0.00, C(19) 0.00, C(20) 0.00, *Cu* −1.42, *N*(2) −1.24

Plane VI (Benzene I)

$-0.3706X + 0.9250Y - 0.1874Z - 2.5578 = 0$

[C(1) 0.02, C(2) −0.04, C(3) 0.02, C(4) 0.03, C(5) −0.06, C(6) 0.03, *Cu* −0.27, *O*(1) 0.02, *N*(1) −0.11, *C*(7) 0.00]

Plane VII (Benzene II)

$-0.4836X + 0.8753Y - 0.0054Z - 6.3325 = 0$

[C(11) 0.07, C(12) −0.010, C(13) 0.06, C(14) 0.01, C(15) −0.04, C(16) 0.00, *Cu* −0.20, *O*(2) −0.06, *N*(2) −0.06, *C*(17) −0.03]

Plane VIII (Saln I)

$-0.3240X + 0.9295Y - 0.1763Z - 2.6213 = 0$

[C(1) 0.02, C(2) −0.05, C(3) −0.00, C(4) 0.03, C(5) −0.05, C(6) 0.05, C(7) 0.04, O(1) 0.03, N(1) −0.06, *Cu* −0.24, *C*(8) −0.16]

Plane IX (Saln II)

$-0.4794X + 0.8774Y - 0.0176Z - 6.0705 = 0$

[C(11) 0.09, C(12) −0.09, C(13) 0.05, C(14) −0.00, C(15) −0.04, C(16) 0.02, C(17) 0.00, O(2) −0.02, N(2) −0.01, *Cu* −0.14, *C*(18) 0.08]

Dihedral angles (°)

I–II	6.7	II–VIII	2.1
I–III	4.1	III–VII	2.6
I–VI	8.8	III–IX	1.8
I–VII	5.5	IV–V	82.7
I–VIII	8.5	IV–VIII	112.1
I–IX	4.9	V–IX	116.6
II–III	10.2	VI–VII	14.0
II–VI	2.7	VIII–IX	13.1

for the rest of the allyl group. The increasing size of the thermal ellipsoids on going from C(8) to C(10) is consistent with the relatively large cavity in which the allyl group lies.

The Ni–N (1.905) and Ni–O (1.844 Å) distances are similar to the corresponding values (1.92 and 1.84 Å) in *trans* planar bis(*N*-isopropyl-3-methylsalicylideneiminato)-[14] and bis(*N*-ethylsalicylideneiminato)-nickel(II),[15] and the mean values (1.91 and 1.83 Å) in bis(*N*-methylsalicylideneiminato)nickel(II).[16] The sum of the angles in the chelate ring falls 7° short of the 720° required for a planar configuration, whereas if the ideal values for σ bonding were preserved the sum of the angles would be 690°.[17] The bite distance N · · · O 2.72 Å is equal to the weighted average[18] for the *trans* planar $[Ni(saln)_2]$ complexes. It is typical of the ranges previously noted for nickel complexes: *ca.* 2.75 for square planar,[19] *ca.* 2.84 for tetrahedral,[20] and *ca.* 2.91 Å for octahedral[21] co-ordination. The benzene ring is essentially planar (Table 5). The five atoms of the chelate ring excluding Ni are remarkably planar, and C(8), the first atom of the allyl group, is also close to this plane. The whole saln unit is planar and its bond lengths and angles (Table 3) are as expected considering the final estimated standard deviations (e.s.d.s). There are no short intermolecular contacts, and because the nearest Ni atoms are more than 7 Å apart and the planes of adjacent molecules are steeply inclined there is no magnetic interaction. This is consistent with the stabilization of the spin-doublet state of Ni^{II} in the solid state, and explains why the compound is diamagnetic in the solid state.

Table 7

Steps (Å) at Ni for salicylaldimine planes in various $[Ni(Rsaln)_2]$ complexes

R	Step		Ref.
	saln I	saln II	
N-Allyl	0.51	−0.51	
[4-Methyl-4-azaheptane-1,7-diylbis(salicylideneiminato)]-nickel	−0.37	0.78	19
N-Isopropyl-3-methyl	−0.38	0.38	14
N-γ-Dimethylaminopropyl	0.39	−0.40	*a*
3-Ethyl-*N*-isopropyl	0.31	0.22	*b*
N-Isopropyl	−0.14	0.20	20
N-t-Butyl	0.05	0.02	*c*
Hexahydrate of [3,6-diazaoctane-1,8-diylbis-(salicylideneiminato)]nickel	−0.33 [d]		*e*
N-Cyclohexyl	−0.65	0.65	33

[a] M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 490. [b] R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **22**, 780. [c] E. E. Castellano, O. J. R. Hodder, G. K. Prout, and P. J. Sadler, *J. Chem. Soc. A*, 1971, 2620. [d] From chelate plane. [e] P. D. Cradwick, M. E. Cradwick, G. G. Dodson, D. Hall, and T. N. Waters, *Acta Crystallogr., Sect. B*, 1972, **28**, 45.

$[Cu(asaln)_2]$.—Figures 3 and 4 depict the [010] and [100] projections of the unit-cell contents, except H atoms, and Figure 5 shows for one molecule the thermal ellipsoids plot at 50% probability and the atomic numbering scheme adopted. It is clear that the molecules form layers parallel to the *xz* plane. The ligands have an approximately *trans*-planar configuration around Cu. The stepping (Table 6) in this case is very small compared to the nickel analogue. The molecule is planar but is slightly distorted so that all parts except the allyl groups conform approximately to two-fold symmetry. The allyl groups are approximately centrosymmetrically related. The co-ordination square is slightly distorted tetrahedrally. Thus, the N and O atoms lie + and −0.05 Å, respectively, from the best plane with Cu 0.02 Å on the O side of the plane. The angles N–Cu–N 178° and O–Cu–O 176° are typical for Cu where slight tetrahedral distortion from a square-planar configuration is often observed.[22] The difference (0.015 Å) between Cu–O(1) and Cu–O(2) is not significant, but that (0.045 Å) between Cu–N(1) and Cu–N(2) is probably just significant. However, the mean values of 2.015 Å for Cu–N and 1.875 Å for Cu–O are in good agreement with those reported in Table 4 of ref. 23 for *trans*-planar copper co-ordination.

The N(1)–C(7) (1.26 Å) and N(2)–C(17) (1.29 Å) bonds are within the range of 1.30 ± 0.04 Å derived for N=C from theoretical calculations.[24] The N(2)–C(17) bond length (1.53 Å) is normal for N–C(8) reported for several copper saln complexes (Table 5 of ref. 25), but N(1)–C(8) (1.57 Å) is large. A study of N–C(8) bond lengths in several metal saln complexes has revealed an interesting feature, namely that this bond length falls into two categories. In the first its value ranges from 1.43 to 1.45 Å when C(8) is a part of an aromatic ring,[26-28] whereas in the second category its value is $\geqslant$1.47 Å when C(8) is part of a linear chain,[15,23,29-32] a cyclohexyl group,[33] ethylenediamine,[34,35] tetramethylenediamine,[36] or a cyclohexanediamine group.[37] The shorter length in the first group might be due to conjugation between the π orbitals of N with the π orbitals of the aromatic ring, which is not possible either for the second set of compounds or in the present two molecules.

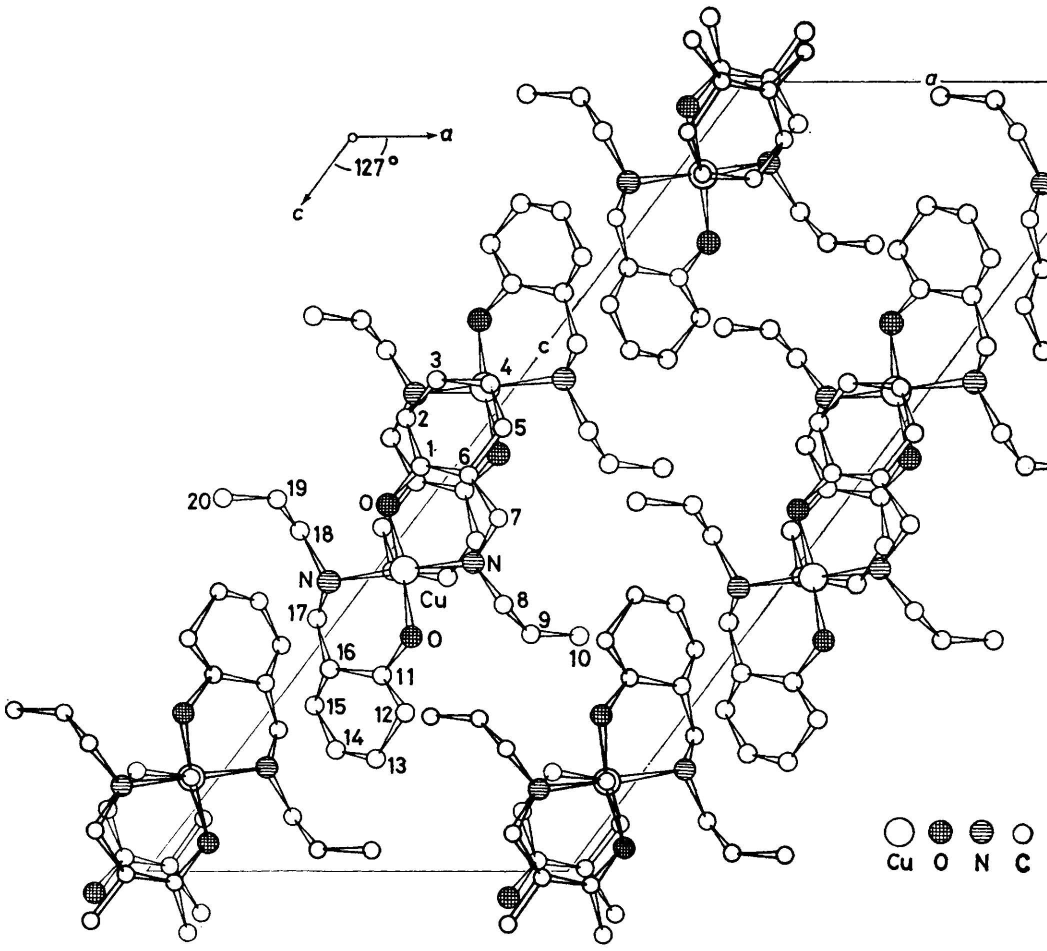

FIGURE 3 Unit-cell contents of [Cu(asaln)$_2$] projected on 010 plane

The Cu–N(1)–C(8) and Cu–N(2)–C(18) angles are equal and compare satisfactorily with the value of 118° in bis(*N*-β-dimethylaminoethylsalicylideneiminato)copper(II)[38] and 120° in bis(*N*-2-pyridylsalicylideneiminato)copper(II).[39] In both the chelate rings the sum of the angles (719°) is close to the 720° required for planarity. The Cu atom lies 0.24 Å below the mean saln I plane and 0.14 Å below the saln II plane. These values compare well with the steps observed in different forms of bis(*N*-ethylsalicylideneiminato)copper(II).[22,40,41] Saln II (plane 9) has a root-mean-square (r.m.s.) deviation of 0.049 Å and is, therefore, a trifle more buckled than its counterpart saln I (plane 8) (0.041 Å). Both saln groups are some what more distorted than that in the nickel complex (0.037 Å). The larger bite distance for N(2) · · · O(2) also points to the same phenomenon. In the copper complex the saln planes are both tilted by *ca.* 7° relative to the co-ordination square and are rotated in opposite directions around the longest axis of the molecule to produce a two-bladed propeller shape. There is ample clearance between C(8) and O(2), *etc.*, but the fact that the two allyl groups are approximately centrosymmetrically related seems to stem from the packing and probably contributes to the minor conformational differences

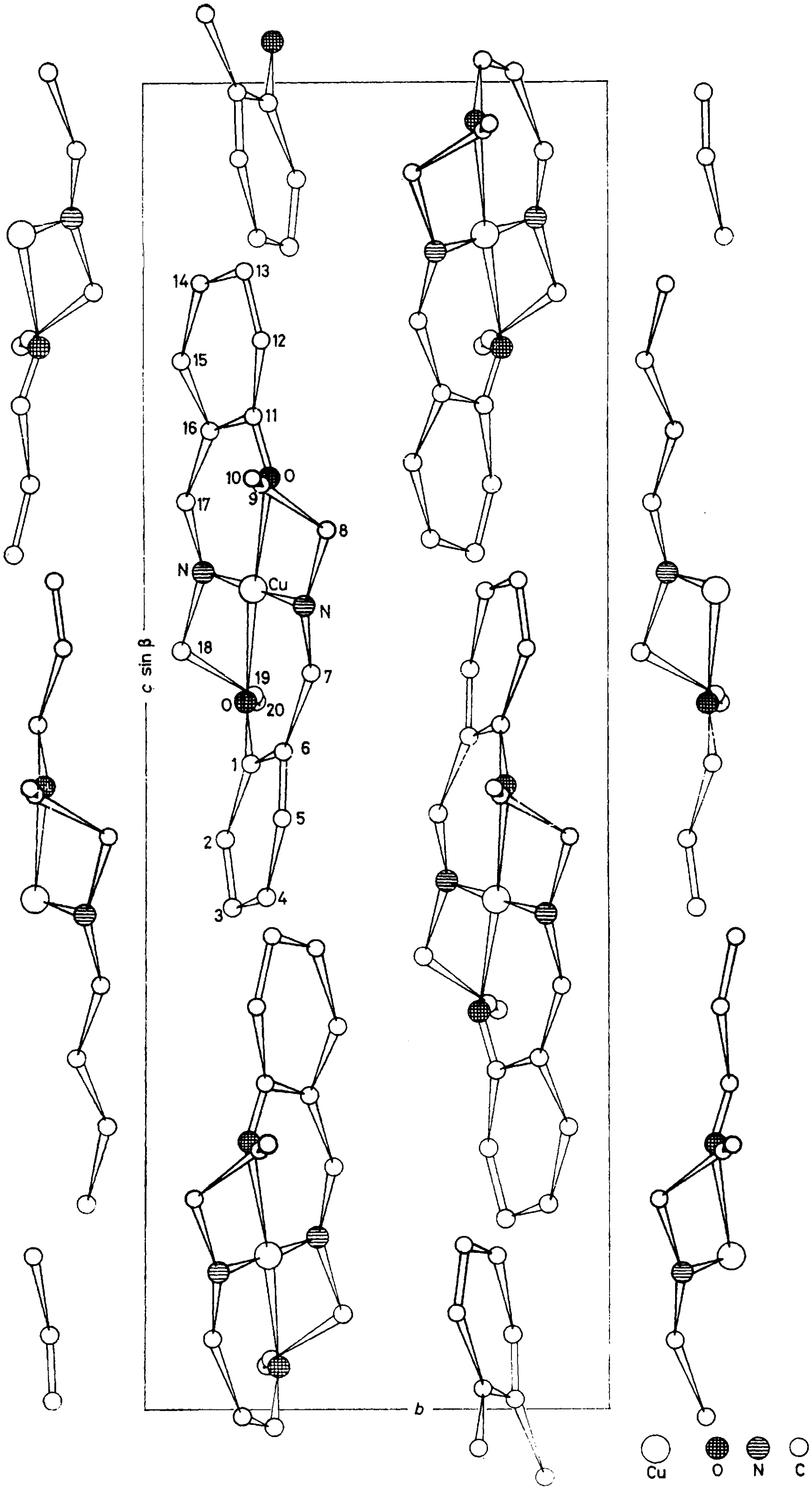

FIGURE 4 [100] Projection of unit-cell contents of [Cu(asaln)$_2$]

between the two saln groups. There are no significantly shorter inter- or intra-molecular distances.

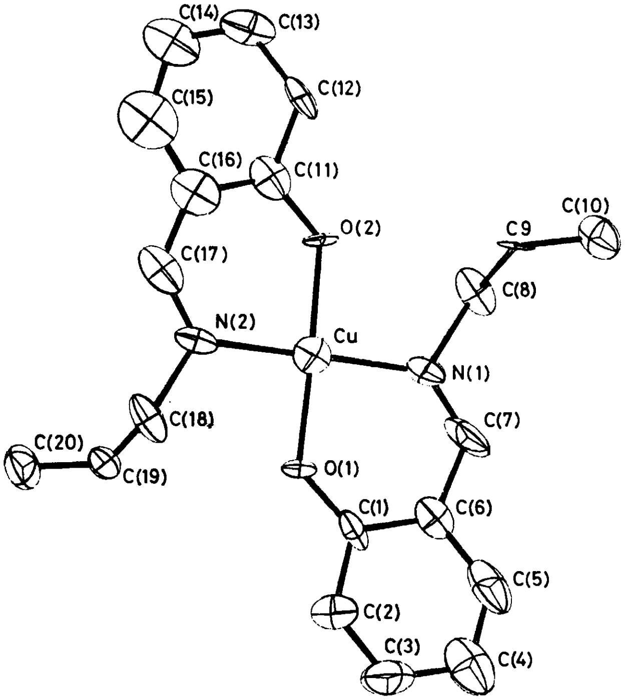

FIGURE 5 Thermal ellipsoid plot at 50% probability and atom-numbering scheme for [Cu(asaln)$_2$]

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