

ion being Δ . Thermal motions of the C atoms of five-membered rings are relatively small, indicating the rigidity of the 1*R*,2*R*-chxn chelate rings. The Ni–N distances and the N–Ni–N angles are common to those of Ni^{II} diamine complexes such as [Ni(en)₃]²⁺ (Swink & Atoji, 1960). All other bond lengths and angles are normal.

The packing of the crystal structure projected along the *c* axis is presented in Fig. 2. A unit cell contains four complex ions, eight Br counter anions, and 12 waters of crystallization. Weak hydrogen bonds are observed between the water molecules and the amino groups and also between the water molecules, which are shown in Fig. 1(b).

In the present crystal-structure determination, it is clear that the five-membered chelate ring of 1*R*,2*R*-chxn adopts a rigid λ *gauche* form even in the substitution-labile Ni^{II} complex. These structural features indicate the reason why the use of chiral 1,2-chxn is effective for the stereochemical regulation of the *N*-glycoside ligands in the Ni^{II} *N*-glycoside complexes (Takahashi *et al.*, 1987). In addition, the assumptions of the configurational and CD spectral assignments of [Ni(1*R*,2*R*-chxn)₃]²⁺ (Treptow, 1968; Harding, Mason & Peart, 1973) are confirmed.

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Structure of the Ordered and Disordered Forms of Aquachloro(2,6-diacetylpyridine disemicarbazone)copper(II) Chloride Dihydrate

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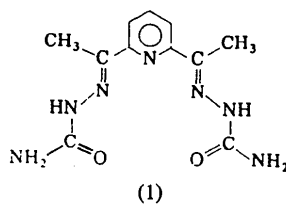
Abstract. The crystal structures of an ordered, (I), and a disordered form, (II), of the seven-coordinate copper complex aquachloro(2,6-diacetylpyridine disemicarbazone)copper(II) chloride dihydrate have been determined. (I) Pale yellow, [Cu(C₁₁H₁₅N₇O₂)Cl(H₂O)]·Cl·2H₂O, *M_r* = 465.82, triclinic, *P*1̄, *a* = 7.093 (4), *b* = 7.768 (3), *c* = 18.477 (12) Å, α = 86.37 (4), β = 84.90 (5), γ = 67.00 (4)°, *V* = 933.0 (9) Å³, *Z* = 2, *D_x* = 1.66 g cm⁻³, *Mo K α* , λ = 0.71093 Å, μ = 15.4 cm⁻¹, *F*(000) = 478, *T* = 300 K, *R* = 0.066 and *wR* = 0.051 for 2471 reflections and 235 parameters.

(II) Golden yellow, [Cu(C₁₁H₁₅N₇O₂)Cl_{*x*}(H₂O)_{2-*x*}]·Cl_{2-*x*}·(*x*+1)H₂O where *x* = 0.974 (6), *M_r* = 465.82, monoclinic, *I*2/a, *a* = 17.980 (5), *b* = 13.192 (2), *c* = 7.956 (4) Å, β = 99.95 (3)°, *V* = 1859 (1) Å³, *Z* = 4, *D_x* = 1.66 g cm⁻³, μ (*Mo K α*) = 15.2 cm⁻¹, *F*(000) = 956, *T* = 300 K, *R* = 0.064 and *wR* = 0.044 for 1637 reflections with 139 parameters. In both cases the cation is seven coordinate. The ligand 2,6-diacetylpyridine disemicarbazone forms a planar pentagon around the central Cu^{II} ion in both structures. In (I) the apical Cl and H₂O are ordered while in (II) the two groups are disordered and the complex cation has twofold symmetry.

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examples involving Cu^{II}. In Cu(NO₃)₂py₃, Cameron, Taylor & Nuttall (1972) found that the bidentate nitrates provided four of the seven donor atoms. Subsequently, Wester & Palenik (1974) reported the pentagonal bipyramidal cation [Cu(dapsc)(H₂O)₂]²⁺, where dapsc is 2,6-diacetylpyridine disemicarbazone, (I). This was followed by Drew, Nelson & Nelson (1981) reporting a pentagonal bipyramidal CuL²⁺ cation with a heptadentate Schiff-base ligand. We have prepared and determined the crystal structures of two pentagonal bipyramidal Cu^{II} complexes. The visually different colors of the two complexes initially led us to believe that they had different axial groups. However, our structural study has demonstrated that one is an ordered and one a disordered structure with the same general features.



Experimental. A mixture of 0.4262 g of CuCl₂ (2.5 mmol), 0.4206 g of 2,6-diacetylpyridine (Aldrich Chemical Co., 97%, 2.5 mmol) and 0.5576 g of semicarbazide hydrochloride (5.0 mmol) in 50 ml of water is heated and stirred for 1 h at 333–343 K. On cooling and slow evaporation of the water, yellow crystals of [Cu(dapsc)(Cl)(H₂O)]Cl·2H₂O, (I), suitable for X-ray studies are formed. If the above mixture is not heated but stirred at room temperature for 2 h and then left standing at room temperature, a yellow solid forms after 7 d. If the solid is filtered off and the water slowly evaporated, golden yellow crystals of the disordered form, (II), suitable for X-ray studies are formed. Calculated for C₁₁H₂₁Cl₂CuN₇O₅: C 28.37; H 4.55; N 21.05%; found: C 28.00; H 4.55; N 20.91%. The golden yellow crystals appeared to be isomorphous with the [MCl(dapsc)(H₂O)]Cl·2H₂O complexes reported by Palenik & Wester (1978). However, some of the intensity differences in the Weissenberg photographs between the zinc and the copper complexes appeared larger than might be expected. Our final results indicate that (II) is disordered (see below) which can explain the observed intensity differences.

Intensity data for both compounds were collected using a Nicolet R3m diffractometer and graphite-monochromatized Mo K α radiation. The experimental details are collected in Table 1. The changes in the intensity variations of the standard reflections were used to derive an empirical decay curve which was applied to the data. We have observed that crystals containing solvent molecules of crystallization will occasionally show large changes in the standard

Table 1. *Experimental data for the crystallographic analysis*

	(I)	(II)
Lattice-parameter measurement		
Number of reflections	25	25
2 θ range (°)	4.4–25.0	12.7–22.1
Crystal size (mm)	0.13 × 0.30 × 0.41	0.12 × 0.37 × 0.37
Radiation used	Mo K α	Mo K α
Scan speed (° min ⁻¹)	2.0–29.3	2.0–24.0
Scan width (°)	±1.12	±1.0
2 θ range (°)	1.5–47.0	2.0–50.0
h range	0–7	±20
k range	±8	0–15
l range	±20	0–9
Number of standard reflections	2 (030, $\bar{1}\bar{3}5$)	2 (242, $2\bar{4}\bar{2}$)
Variation (±%, ± σ)	12, 5	3, 1.7
Number of measured (unique) reflections	3024 (2762)	3624 (1785)
R _{int}	0.05 (5)	0.01 (2)
Condition for observed reflections	F _o ≥ 2 σ (F _o)	F _o ≥ 2 σ (F _o)
Number of reflections used in refinement	2471	1637
(d/ σ) _{max}	0.02	0.03
Min. max. $\Delta\rho$ (e Å ⁻³)	–0.65, 0.56	–0.75, 0.68
Number of parameters refined	235	139
R	0.066	0.064
wR	0.051	0.044
S	3.86	3.77

Table 2. *Atomic coordinates (× 10⁴) and equivalent isotropic thermal parameters (Å² × 10³)*

	x	y	z	U _{eq} *
(I)				
Cu	507 (1)	3224 (1)	3230 (1)	41 (1)
Cl(1)	3708 (2)	3655 (2)	3769 (1)	50 (1)
Cl(2)	3112 (4)	5556 (3)	–1204 (1)	97 (1)
Ow(1)	–2311 (7)	3088 (5)	2786 (2)	56 (2)
N(1)	–109 (7)	5626 (6)	2679 (3)	35 (2)
C(1)	547 (9)	5620 (8)	1986 (3)	38 (3)
C(2)	78 (11)	7299 (9)	1577 (4)	53 (3)
C(3)	–1033 (12)	8926 (9)	1920 (4)	61 (4)
C(4)	–1735 (10)	8936 (8)	2631 (4)	48 (3)
C(5)	–1259 (9)	7220 (7)	3024 (3)	35 (2)
C(6)	1736 (9)	3710 (8)	1699 (3)	43 (3)
C(7)	2474 (11)	3418 (9)	928 (4)	62 (3)
N(2)	1971 (7)	2432 (6)	2215 (3)	41 (2)
N(3)	3004 (7)	565 (6)	2059 (3)	44 (2)
C(8)	3061 (9)	–613 (9)	2651 (4)	44 (3)
O(1)	2281 (7)	–12 (6)	3246 (2)	54 (2)
N(4)	4034 (8)	–2423 (7)	–2516 (3)	54 (2)
C(9)	–1969 (9)	6982 (7)	3777 (3)	37 (2)
C(10)	–3244 (10)	8599 (8)	4232 (4)	50 (3)
N(5)	–1420 (7)	5229 (5)	3970 (3)	32 (2)
N(6)	–1974 (7)	4724 (6)	4643 (3)	37 (2)
C(11)	–1316 (9)	2808 (7)	4776 (3)	40 (3)
O(2)	–304 (7)	1738 (5)	4289 (2)	52 (2)
N(7)	–1875 (8)	2277 (6)	5426 (3)	51 (2)
Ow(2)	5139 (8)	–1401 (6)	766 (3)	77 (3)
Ow(3)	1986 (10)	–1213 (8)	–150 (4)	125 (3)
(II)				
Cu	2500	10419 (1)	0	45 (1)
Cl(a)†	3433 (2)	10288 (3)	2919 (4)	44 (1)
Ow(a)‡	3183 (4)	10627 (7)	2200 (11)	39 (3)
Cl(b)†	4559 (2)	9294 (2)	3236 (4)	50 (1)
Ow(b)†	4991 (6)	9225 (6)	3636 (11)	61 (3)
Ow(2)	2500	11250 (4)	5000	121 (3)
N(1)	2500	8790 (4)	0	35 (2)
C(1)	1936 (2)	8273 (3)	535 (5)	32 (1)
C(2)	1915 (2)	7229 (3)	538 (5)	39 (2)
C(3)	2500	6717 (4)	0	43 (2)
C(4)	1368 (2)	8962 (3)	1127 (5)	34 (1)
C(5)	677 (2)	8533 (4)	1676 (6)	50 (2)
N(2)	1536 (2)	9889 (2)	1122 (4)	33 (1)
N(3)	1082 (2)	10622 (3)	1614 (4)	38 (1)
C(6)	1350 (2)	11586 (3)	1555 (5)	40 (1)
O(1)	1914 (1)	11784 (2)	918 (4)	46 (1)
N(4)	933 (2)	12295 (3)	2174 (5)	54 (1)

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

† s.o.f. = 0.487 (6).

‡ s.o.f. = 0.513 (6).

reflections with time. These cases will usually have somewhat higher final R values. No absorption corrections were made because of the small values of μ and the fact that the crystal was mounted perpendicular to the plate. The structures were both solved using Patterson and Fourier syntheses. For (II) various ordered models in Ia were considered first. The poor refinement, unsatisfactory thermal parameters, rela-

tively high R values and large peaks of 2 to 3 $e \text{ \AA}^{-3}$ in the difference Fourier maps all suggested a disordered model in $I2/a$. In $I2/a$ the refinement of the disordered model proceeded smoothly. The site-occupancy factor, s.o.f. in Table 2, was refined from an initial value of 0.5 for the disordered waters and chloride ions. With one exception [H(42N)], all the H atoms were located in difference Fourier syntheses. The H atoms in (I) and (II) were given a U_{iso} based on the mean value of B_{iso} from the isotropic refinement plus 1. The H-atom contributions were included in the calculations but their parameters were not refined. The refinement was by blocked cascade least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [\sigma(F_o)]^{-2}$. The scattering factors used were those in the *SHELXTL* package and are the analytical form given in *International Tables for X-ray Crystallography* (1974). All calculations were performed using the *SHELXTL* package (Sheldrick, 1986). The final positional parameters are given in Table 2 with the bond distances and dihedral angles given in Table 3.* A view of the ordered cation is given in Fig. 1.

Table 3. Bond lengths (\AA), angles between normals to planes ($^\circ$) and hydrogen-bond geometry

(I)		(II)	
Cu-Cl(1)	2.701 (2)	Cu-Cl(a)	2.625 (3)
Cu-Ow(1)	2.269 (5)	Cu-Ow(a)	1.976 (8)
Cu-N(1)	1.978 (4)	Cu-N(1)	2.148 (5)
Cu-N(2)	2.068 (5)	Cu-N(2)	2.196 (3)
Cu-O(1)	2.330 (4)	Cu-O(1)	2.269 (3)
Cu-N(5)	2.107 (4)		
Cu-O(2)	2.351 (4)		
N(1)-C(1)	1.321 (7)	N(1)-C(1)	1.350 (4)
N(1)-C(5)	1.351 (6)		
C(1)-C(2)	1.402 (9)	C(1)-C(2)	1.377 (6)
C(1)-C(6)	1.495 (8)	C(1)-C(4)	1.502 (5)
C(2)-C(3)	1.362 (9)	C(2)-C(3)	1.380 (5)
C(3)-C(4)	1.361 (11)		
C(4)-C(5)	1.410 (8)		
C(5)-C(9)	1.463 (8)		
C(6)-C(7)	1.475 (9)	C(4)-C(5)	1.497 (6)
C(6)-N(2)	1.304 (8)	C(4)-N(2)	1.260 (5)
N(2)-N(3)	1.381 (6)	N(2)-N(3)	1.367 (5)
N(3)-C(8)	1.374 (8)	N(3)-C(6)	1.363 (6)
C(8)-O(1)	1.220 (8)	C(6)-O(1)	1.238 (5)
C(8)-N(4)	1.331 (8)	C(6)-N(4)	1.344 (6)
C(9)-C(10)	1.487 (8)		
C(9)-N(5)	1.297 (7)		
N(5)-N(6)	1.352 (7)		
N(6)-C(11)	1.387 (7)		
C(11)-O(2)	1.235 (7)		
C(11)-N(7)	1.324 (8)		

Angles between normals to planes ($^\circ$)	
(I)	
Pyridine ring plane-plane [C(6)N(2)N(3)C(8)O(1)]	2.5 (7)
Pyridine ring plane-plane [C(9)N(5)N(6)C(11)O(2)]	5.5 (8)
Plane [C(6)N(2)N(3)C(8)O(1)]-plane [C(9)N(5)N(6)C(11)O(2)]	7.1 (9)
(II)	
Pyridine ring plane-plane [C(4)N(2)N(3)C(6)O(1)]	4.4 (8)
Plane [C(4)N(2)N(3)C(6)O(1)]-plane [C(4)N(2)N(3)C(6)O(1)]	7.8 (8)

Symmetry code: (i) $0.5-x, y, -z$.

Hydrogen-bond geometry				
D-H	A	D...A (\AA)	A...H (\AA)	\angle D-H...A ($^\circ$)
(I)				
N(3)-H(3N)	Ow(2)(x, y, z)	2.888 (7)	1.92	144
N(6)-H(6N)	Cl(1)($-x, 1-y, 1-z$)	3.212 (5)	2.19	155
N(7)-H(71N)	Cl(1)($-x, 1-y, 1-z$)	3.306 (5)	2.46	143
N(7)-H(72N)	O(1)($-x, -y, 1-z$)	2.987 (8)	2.18	143
N(7)-H(72N)	O(2)($-x, -y, 1-z$)	2.926 (7)	2.14	137
Ow(1)-H(1w)	Cl(2)($-x, 1-y, -z$)	3.068 (6)	2.10	150
Ow(1)-H(2w1)	Cl(1)($-1+x, y, z$)	3.111 (6)	2.03	164
Ow(2)-H(1w2)	Cl(2)($1-x, -y, -z$)	3.054 (6)	2.30	133
Ow(2)-H(2w2)	Ow(3)(x, y, z)	2.877 (9)	1.82	134
Ow(3)-H(1w3)	Ow(3)($-x, -y, -z$)	2.739 (9)	1.67	157
Ow(3)-H(2w3)	Cl(2)($x, -1+y, z$)	3.083 (6)	1.96	142
(II)				
N(3)-H(3N)	Ow(b)($-0.5+x, 2-y, z$)	2.751 (6)	1.90	144
	Cl(b)	3.224 (4)	2.30	155
N(4)-H(1N4)	Ow(a)($0.5-x, 2.5-y, 0.5-z$)	3.165 (6)	2.28	167
	Cl(a)	3.391 (5)	2.56	155
Ow(a)-H(1wa)	Ow(2)(x, y, z)	2.845 (8)	2.14	167
Ow(a)-H(2wa)	Cl(b)(x, y, z)	3.032 (5)	2.52	140
Ow(b)-H(1wb)	Cl(a)(x, y, z)	3.095 (5)	2.45	130
Ow(b)-H(2wb)	Ow(b)($1-x, 2-y, 1-z$)	2.977 (7)	2.09	138
	Cl(b)	3.157 (6)	2.17	153
Ow(2)-H(1w2)	Cl(a)(x, y, z)	2.849 (5)	2.27	149

Discussion. Although the two cations are chemically identical, there are surprising differences in the bond lengths in the two cations. In the ordered form, (I), the Cu-Cl distance of 2.707 (2) \AA and the Cu-Ow(1) distance of 2.269 (5) \AA are significantly longer than those observed in the disordered form, (II), of 2.625 (3) and 1.976 (6) \AA respectively. The lengthening of the axial bonds is accompanied by a decrease in Cu-N bond lengths in the equatorial plane [N(1) 1.978 (4); N(2) 2.069 (5); N(5) 2.109 (4) \AA] compared to those in the disordered form (II) [N(1) 2.148 (5); N(2) = N(5) = 2.196 (3) \AA]. However, the Cu-O (equatorial) distances are longer in the ordered form

* Lists of anisotropic thermal parameters, bond angles, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44398 (35 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

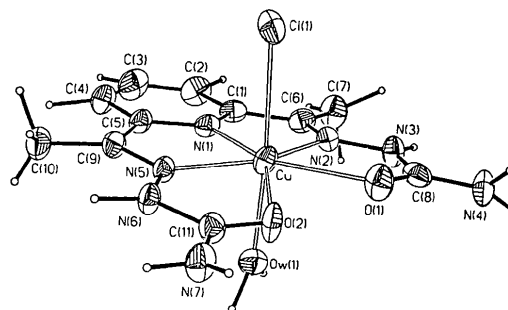


Fig. 1. A view of the ordered cation aquachloro(2,6-diacetylpyridine disemicarbazone)copper(II). The thermal ellipsoids are at 35% probability.

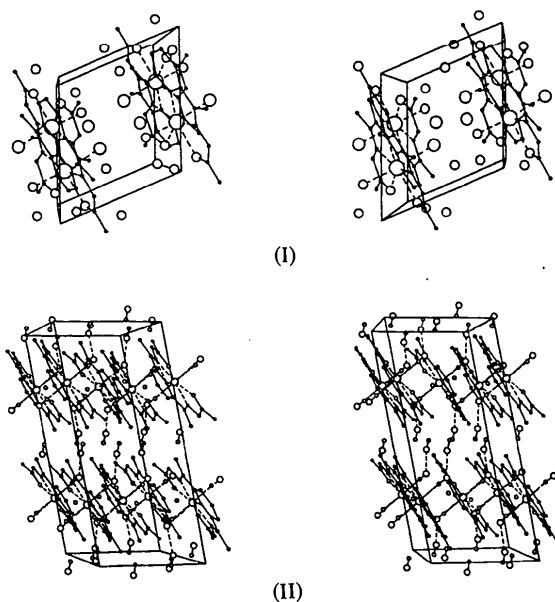


Fig. 2. A stereo packing diagram of the ordered, (I), and disordered structures, (II).

[O(1) 2.330 (4); O(2) 2.351 (4) Å] than in the disordered form [O(1) = O(2) = 2.269 (3) Å]. The differences in the dimensions of the two cations may be related to the difference in hydrogen-bonding patterns in the two crystals (Table 3, Fig. 2). In the ordered structure, (I), on semicarbazone chain forms only one hydrogen bond while the other chain is involved in four hydrogen bonds. However, in (II), both semicarbazone chains form two hydrogen bonds involving the disordered chloride ion and water molecule. In both (I)

and (II) all the H atoms on the water molecules form hydrogen bonds but the hydrogen bonds to the water molecules are different. The differences in the packing in the two cases lead to a slightly higher density for the ordered structure compared to the disordered one. The formation of the disordered form (II) occurs at room temperature while the ordered form (I) comes from the heated solutions. Consequently, the rate of conversion of (II) to (I) is slow. Redissolving (II) will produce (I) but other reactions occur so that the result is a mixture of products. We are currently investigating these reactions.

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Complexes of Cadmium(II) Bromide and Cadmium(II) Iodide with 18-Crown-6 Ether*

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Abstract. [Cd(C₁₂H₂₄O₆)Br₂], *M_r* = 536.5, rhombohedral, *R* $\bar{3}$, *a* = 11.8127 (13), *c* = 11.9464 (15) Å (hexagonal setting), *V* = 1443.7 (4) Å³, *Z* = 3, *D_x* = 1.851 (1) Mg m⁻³, Mo *K*α, λ = 0.71073 Å, μ = 5.261 (1) mm⁻¹, *F*(000) = 786, *T* = 293 K, *R* = 0.028, *wR* = 0.031 for 528 reflexions [*I* > 3σ(*I*)] and 50

variables. [Cd(C₁₂H₂₄O₆)I₂], *M_r* = 630.5, orthorhombic, *Pnma*, *a* = 16.563 (3), *b* = 27.996 (5), *c* = 8.382 (2) Å, *V* = 3887 (1) Å³, *Z* = 8, *D_x* = 2.155 (1) Mg m⁻³, Mo *K*α, λ = 0.71073 Å, μ = 4.283 (2) mm⁻¹, *F*(000) = 2384, *T* = 294 K, *R* = 0.037, *wR* = 0.039 for 1287 reflexions [*I* > 3σ(*I*)] and 201 variables. The CdBr₂ complex is isostructural with the corresponding CdCl₂ and HgCl₂ compounds [Paige & Richardson (1984). *Can. J. Chem.* **62**, 332–335],

* 1,4,7,10,13,16-Hexaoxacyclooctadecane.