

Crystal and Molecular Structure of 2,6-Diacetylpyridine Bis(picolinoylhydrazone) Hemihydrate

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Abstract

Crystals of the title compound are monoclinic, space group $C2/c$ with unit-cell dimensions: $a = 28.14$ (2), $b = 10.09$ (1), $c = 14.84$ (1) Å, $\beta = 103.1$ (1)° and $Z = 8$. The structure was solved from X-ray diffractometer data by direct methods and refined by a least-squares method to $R = 6.6\%$ for 2836 independent reflections. The molecule shows approximate twofold symmetry.

Introduction

Metal complexes of polydentate ligands containing the $-C(O)NN=CC=N-$ system have been widely investigated in our laboratory (Nardelli, Pelizzi & Pelizzi, 1977*b*). Among these ligands, 2,6-diacetylpyridine bis(picolinoylhydrazone) (hereinafter H_2DIP) has been examined in two divalent transition-metal complexes, $Cu_2(DIP)Cl_2 \cdot H_2O$ (Mangia, Pelizzi & Pelizzi, 1974) and $MnCl_2(H_2DIP) \cdot 5H_2O$ (Nardelli, Pelizzi & Pelizzi, 1977*a*). Continuing this research work we have now examined by X-ray diffractometry the free H_2DIP molecule with the aim of investigating the structural differences between the complexed and uncomplexed forms.

The title compound, obtained by condensation of 2,6-diacetylpyridine and picolinohydrazide in water-ethanol, occurs as pale-yellow tabular crystals. Optical properties, and rotation and Weissenberg photographs indicated that the crystals are monoclinic. From these photographs preliminary unit-cell dimensions were also obtained, while a fairly accurate determination has been

achieved by measuring the setting angles for twenty reflections on an automated Siemens AED single-crystal diffractometer. The most significant crystal data are collected in Table 1.

A quarter of the reciprocal sphere was scanned in the range $4.0 < 2\theta < 140.0^\circ$ by use of the $\omega-2\theta$ scanning technique with Ni-filtered $Cu K\alpha$ radiation. Of the 3889 independent reflections recorded, 2836 were considered as observed having $I > 2\sigma(I)$. A standard reflection was monitored every twenty reflections as a test on crystal and instrument stability and no systematic change was observed in its intensity during data collection. After the usual data reduction, the structure

Table 2. Fractional atomic coordinates ($\times 10^4$), with standard deviations, for non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	-836 (1)	143 (3)	5281 (2)
O(2)	2264 (1)	8513 (3)	7401 (2)
N(1)	718 (1)	4463 (3)	5285 (2)
N(2)	-160 (1)	1918 (3)	4989 (2)
N(3)	-426 (1)	1132 (3)	4299 (2)
N(4)	-1014 (1)	17 (3)	2841 (2)
N(5)	1578 (1)	6908 (3)	6262 (2)
N(6)	1865 (1)	7832 (3)	5957 (2)
N(7)	2363 (1)	9452 (3)	5144 (2)
C(1)	424 (1)	3548 (3)	5526 (2)
C(2)	360 (1)	3411 (4)	6436 (2)
C(3)	614 (1)	4277 (5)	7104 (2)
C(4)	916 (1)	5227 (4)	6861 (2)
C(5)	962 (1)	5290 (4)	5943 (2)
C(6)	162 (1)	2678 (4)	4763 (2)
C(7)	281 (2)	2759 (4)	3827 (3)
C(8)	-770 (1)	315 (4)	4504 (2)
C(9)	-1073 (1)	-368 (4)	3667 (2)
C(10)	-1403 (1)	-1314 (4)	3794 (3)
C(11)	-1696 (2)	-1897 (4)	3016 (3)
C(12)	-1647 (2)	-1494 (5)	2164 (3)
C(13)	-1308 (2)	-561 (5)	2100 (3)
C(14)	1275 (1)	6289 (3)	5622 (2)
C(15)	1208 (1)	6511 (4)	4600 (2)
C(16)	2192 (1)	8579 (3)	6562 (2)
C(17)	2461 (1)	9535 (3)	6074 (2)
C(18)	2779 (1)	10440 (4)	6581 (2)
C(19)	3014 (1)	11321 (4)	6117 (3)
C(20)	2919 (2)	11236 (4)	5169 (3)
C(21)	2598 (2)	10308 (4)	4710 (3)
O(3)	0	-353 (13)	2500

Table 1. Crystallographic data

$C_{21}H_{19}N_7O_2 \cdot \frac{1}{2}H_2O$	$\beta = 103.1$ (1)°
Monoclinic	$U = 4104$ Å ³
Space group: $C2/c$ from systematic absences and structural analysis	$Z = 8$
$M_r = 410.45$	$D_c = 1.33$ Mg m ⁻³
$a = 28.14$ (2) Å	$F(000) = 1720$
$b = 10.09$ (1)	$\lambda(Cu K\alpha) = 1.5418$ Å
$c = 14.84$ (1)	$\mu(Cu K\alpha) = 0.75$ mm ⁻¹

amplitudes were put on an absolute scale by comparing observed and calculated values. The crystal used for the data collection was a thin tablet with a mean radius of 0.11 mm; no correction for absorption was made.

The structure has been solved by direct methods (Germain, Main & Woolfson, 1971) and refined by block-diagonal least-squares calculations, first with isotropic and then with anisotropic (excepting the O atom from the water molecule) thermal parameters for the non-hydrogen atoms. The quantity minimized was $\sum w(\Delta F)^2$ with unit weights. All the H atoms belonging to the organic molecule have been located on a Fourier difference map and their contributions were allowed for in the calculations assuming isotropic parameters. Any attempt to locate the H atoms from H₂O was unsuccessful. The final *R* was 0.066 for the observed reflections and 0.082 for the complete set of data. The final atomic parameters are given in Table 2 for the non-hydrogen atoms and in Table 3 for the H atoms. Atomic scattering factors were taken from Cromer & Mann (1968) for O, N and C and from Stewart,

Davidson & Simpson (1965) for H.* All the calculations were performed on the Cyber 76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

Discussion

The molecular shape of the compound is depicted in Fig. 1. The three aromatic rings are strictly planar with no significant departure from the regular geometry. Two of these rings are connected to the third ring

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33839 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates ($\times 10^3$), with standard deviations, for hydrogen atoms

	x	y	z
H(2)	8 (2)	274 (6)	673 (4)
H(3)	53 (2)	418 (6)	785 (4)
H(4)	111 (2)	584 (6)	737 (4)
H(10)	-143 (2)	-145 (6)	452 (4)
H(11)	-191 (2)	-260 (6)	310 (4)
H(12)	-187 (2)	-185 (6)	152 (4)
H(13)	-122 (2)	-15 (6)	161 (4)
H(18)	283 (2)	1049 (6)	725 (4)
H(19)	324 (2)	1207 (6)	647 (4)
H(20)	310 (2)	1181 (6)	486 (4)
H(21)	250 (2)	1024 (6)	412 (4)
H(31)	-40 (2)	121 (6)	361 (4)
H(61)	184 (2)	796 (6)	530 (4)
H(71)	55 (2)	334 (6)	377 (4)
H(72)	0 (2)	304 (6)	325 (4)
H(73)	37 (2)	182 (6)	358 (4)
H(151)	99 (2)	592 (6)	422 (4)
H(152)	154 (2)	630 (6)	436 (4)
H(153)	113 (2)	736 (6)	441 (4)

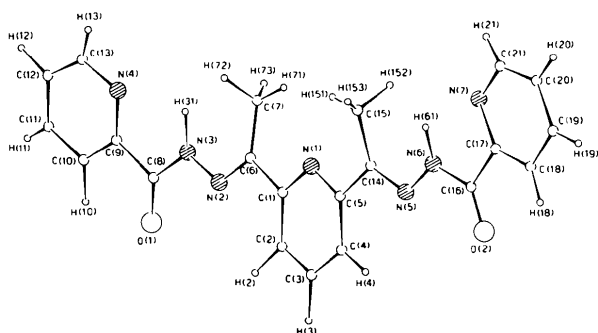


Fig. 1. Clinographic projection of the structure.

Table 4. Bond distances (Å)

N(4)—C(9)	1.332 (5)	N(7)—C(17)	1.347 (4)
C(9)—C(10)	1.374 (6)	C(17)—C(18)	1.377 (5)
C(10)—C(11)	1.388 (5)	C(18)—C(19)	1.381 (6)
C(11)—C(12)	1.365 (6)	C(19)—C(20)	1.374 (6)
C(12)—C(13)	1.359 (7)	C(20)—C(21)	1.370 (6)
C(13)—N(4)	1.350 (6)	C(21)—N(7)	1.338 (6)
C(9)—C(8)	1.505 (5)	C(17)—C(16)	1.509 (5)
C(8)—O(1)	1.221 (5)	C(16)—O(2)	1.217 (4)
C(8)—N(3)	1.357 (5)	C(16)—N(6)	1.359 (4)
N(3)—N(2)	1.375 (4)	N(6)—N(5)	1.376 (4)
N(2)—C(6)	1.288 (5)	N(5)—C(14)	1.285 (4)
C(6)—C(7)	1.503 (6)	C(14)—C(15)	1.502 (5)
C(6)—C(1)	1.489 (5)	C(14)—C(5)	1.486 (5)
C(1)—N(1)	1.341 (5)	C(5)—N(1)	1.348 (5)
C(1)—C(2)	1.409 (5)	C(5)—C(4)	1.399 (5)
C(2)—C(3)	1.391 (5)	C(4)—C(3)	1.382 (6)

Table 5. Bond angles (°)

C(9)—N(4)—C(13)	116.3 (7)	C(17)—N(7)—C(21)	116.4 (7)
N(4)—C(13)—C(12)	123.6 (9)	N(7)—C(21)—C(20)	122.9 (8)
C(13)—C(12)—C(11)	119.4 (9)	C(21)—C(20)—C(19)	120.3 (8)
C(12)—C(11)—C(10)	118.6 (8)	C(20)—C(19)—C(18)	117.8 (8)
C(11)—C(10)—C(9)	118.2 (7)	C(19)—C(18)—C(17)	118.7 (7)
C(10)—C(9)—N(4)	123.9 (8)	C(18)—C(17)—N(7)	123.9 (7)
C(10)—C(9)—C(8)	118.6 (7)	C(18)—C(17)—C(16)	119.8 (7)
N(4)—C(9)—C(8)	117.4 (6)	N(7)—C(17)—C(16)	116.3 (6)
C(9)—C(8)—O(1)	122.4 (7)	C(17)—C(16)—O(2)	122.7 (7)
C(9)—C(8)—N(3)	113.1 (6)	C(17)—C(16)—N(6)	112.1 (5)
O(1)—C(8)—N(3)	124.5 (7)	O(2)—C(16)—N(6)	125.2 (6)
C(8)—N(3)—N(2)	118.6 (6)	C(16)—N(6)—N(5)	121.3 (6)
N(3)—N(2)—C(6)	116.5 (6)	N(6)—N(5)—C(14)	115.3 (6)
C(7)—C(6)—N(2)	126.2 (8)	C(15)—C(14)—N(5)	125.7 (7)
C(1)—C(6)—C(7)	119.7 (6)	C(5)—C(14)—C(15)	118.5 (6)
C(1)—C(6)—N(2)	114.1 (6)	C(5)—C(14)—N(5)	115.8 (6)
C(6)—C(1)—N(1)	115.6 (6)	C(14)—C(5)—N(1)	115.4 (6)
C(6)—C(1)—C(2)	121.5 (7)	C(14)—C(5)—C(4)	122.4 (7)
N(1)—C(1)—C(2)	122.9 (7)	N(1)—C(5)—C(4)	122.2 (7)
C(1)—C(2)—C(3)	117.7 (7)	C(5)—C(4)—C(3)	118.9 (7)
C(1)—N(1)—C(5)	118.5 (6)	C(4)—C(3)—C(2)	119.8 (8)

through two equivalent $-\text{C}(\text{O})\text{NNC}(\text{CH}_3)-$ chains, so two chemically equivalent, crystallographically independent moieties are present, in which corresponding bond lengths and angles are not significantly different as can be seen from Tables 4 and 5. In both chains the values of the bond lengths as well as those of the torsion angles (Table 6) suggest some π -delocalization in the central part, with a preference for a localization of the double bond between N(2) and C(6) (1.288 Å), and N(5) and C(14) (1.285 Å).

The coordinating behaviour of H_2DIP towards Cu and Mn in the related complexes is different: the ligand is anionic and octadentate in $\text{Cu}_2(\text{DIP})\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Mangia, Pelizzi & Pelizzi, 1974) and neutral and penta-dentate in $\text{MnCl}_2(\text{H}_2\text{DIP}) \cdot 5\text{H}_2\text{O}$ (Nardelli, Pelizzi & Pelizzi, 1977a). Comparison of the structural situation of H_2DIP in its uncomplexed and complexed forms shows that bond lengths and angles are little influenced by coordination, in spite of the different conformations of the two $-\text{C}(\text{O})\text{NN}=\text{CC}=\text{N}-$ systems: they are both almost planar in H_2DIP and in $\text{MnCl}_2(\text{H}_2\text{DIP}) \cdot 5\text{H}_2\text{O}$, while in $\text{Cu}(\text{DIP})\text{Cl}_2 \cdot \text{H}_2\text{O}$ one of them is twisted about the N–N bond. Unlike X-ray structural parameters, significant differences are observed in the main vibrational bands of the free H_2DIP as compared with those in the metal complexes, the stretching mode of the C–O bond being the vibration

Table 6. *Some torsion angles* ($^\circ$)

C(5)–C(14)–N(5)–N(6)	180	N(3)–N(2)–C(6)–C(1)	–178
C(14)–N(5)–N(6)–C(16)	–178	C(8)–N(3)–N(2)–C(6)	180
N(5)–N(6)–C(16)–C(17)	179	C(9)–C(8)–N(3)–N(2)	–173

Table 7. *Some intermolecular contacts* (<3.50 Å)

N(3)···O(3)	3.501 (7)	O(2)···C(19 ⁱⁱⁱ)	3.335 (5)
N(4)···O(3)	3.032 (6)	O(1)···C(6 ^{iv})	3.429 (5)
O(1)···C(13 ⁱ)	3.295 (7)	O(1)···C(7 ^{iv})	3.439 (6)
O(2)···C(11 ⁱⁱ)	3.293 (5)	N(2)···C(8 ^{iv})	3.406 (5)
O(2)···C(18 ⁱⁱⁱ)	3.463 (5)	C(20)···C(20 ^v)	3.433 (7)

Superscripts refer to the following equivalent positions:

(i) $x, -y, \frac{1}{2} + z$	(iv) $-x, -y, 1 - z$
(ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	(v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
(iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$	

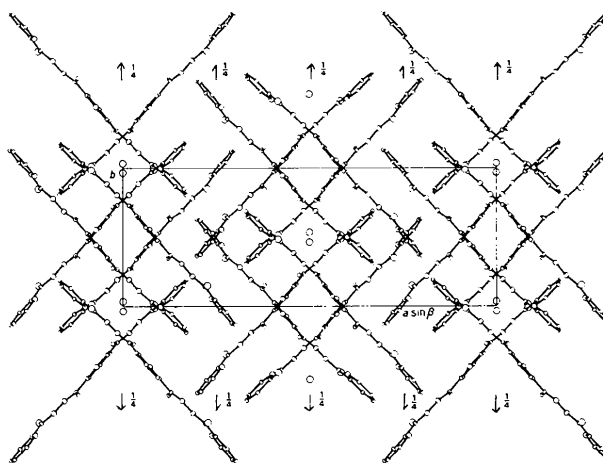


Fig. 2. Diagrammatic projection of the structure along [001] showing the crystal packing.

mainly influenced by complexation [170 cm^{-1} in H_2DIP ; $164, 163 \text{ cm}^{-1}$ in $\text{Cu}_2(\text{DIP})\text{Cl}_2 \cdot \text{H}_2\text{O}$; 165 cm^{-1} in $\text{MnCl}_2(\text{H}_2\text{DIP}) \cdot 5\text{H}_2\text{O}$].

Fig. 2 shows the molecular packing which is characterized by the arrangement of the almost planar organic molecules in stacks parallel to (310) and $(\bar{3}10)$, the angle between these stacks being 93° . Packing interactions, the most significant of which are given in Table 7, also involve a water molecule lying on a twofold axis.

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