

sky, Kowalski & Avery, 1974; Thoennes, Wilkins & Trahanovsky, 1974). For example, the C(19) methyl proton n.m.r. shift data are, respectively, $\delta_{\text{H}} = -0.38$ and $\delta_{\text{H}} = -0.08$ [$\delta(\text{TMS}) = 0.00$] for $\text{C}_{20}\text{H}_{24}$ and $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$, indicating markedly increased proton shielding in the former. The distance of C (19) from the best least-squares plane containing the ten naphthalene atoms is 3.06 Å for $\text{C}_{20}\text{H}_{24}$ and 3.13 Å for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$.* The decrease (0.07 Å) in the C (19)-naphthalene plane distance between the two molecules cannot account for the large observed chemical shift difference on the basis of calculated tables of ring current shielding for proton shifts (Haigh & Mallion, 1972). The chromium tricarbonyl group obviously affects the ring current causing these shifts by withdrawing electron density from the aromatic ring in a manner which awaits detailed elucidation on the basis of the present, and other, structural and spectroscopic data.

The naphthalene ring (ring *A*) associated with the $\text{Cr}(\text{CO})_3$ group in the complex is expanded slightly with respect to the same ring *A* in $\text{C}_{20}\text{H}_{24}$. The corresponding bond distances in the complex are:

C(7)–C(8)	1.405 (8) Å	C(9)–C(10)	1.426 (8) Å
C(7)–C(16)	1.400 (8)	C(10)–C(15)	1.439 (8)
C(8)–C(9)	1.365 (8)	C(15)–C(16)	1.450 (6)

The conformation of the substituted cyclohexane ring is nearly the same for both structures. Torsion angles for this ring are listed in Table 2 and may be compared with other similar structures (Pettersen, Cullen, Pearce, Shapiro & Shapiro, 1974). Table 3 lists the interatomic distances for the hydrocarbon structure. There are no intermolecular carbon-carbon contacts less than 3.70 Å. A supplementary table of valency angles has been deposited along with the structure factor tables.

* Maximum deviations of the ten naphthalene atoms contained in the best least-squares planes are 0.032 Å [C(16)] for $\text{C}_{20}\text{H}_{24}$ and 0.069 Å [C(16)] for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$. The respective r.m.s. deviations are 0.017 and 0.049 Å.

Table 2. Cyclohexane ring torsion angles for $\text{C}_{20}\text{H}_{24}$ *

C(6)–C(1)–C(2)–C(3)	74.4 (3)°
C(1)–C(2)–C(3)–C(4)	–73.9 (3)
C(2)–C(3)–C(4)–C(5)	54.3 (4)
C(3)–C(4)–C(5)–C(6)	–32.9 (4)
C(4)–C(5)–C(6)–C(1)	32.5 (4)
C(5)–C(6)–C(1)–C(2)	–55.1 (3)

* The torsion angle $W(\text{JJKL})$ is defined as the angle between the vector *JI* and the vector *KL* when viewed along *JK*. The sign of *W* is positive if *JI* is to be rotated clockwise into *KL* and negative if anticlockwise.

Table 3. Interatomic distances for $\text{C}_{20}\text{H}_{24}$

Bond	Distance	Bond	Distance
C(1)–C(2)	1.504 (6) Å	C(7)–C(8)	1.403 (5) Å
C(1)–C(6)	1.545 (5)	C(7)–C(16)	1.368 (5)
C(1)–C(7)	1.510 (5)	C(8)–C(9)	1.363 (5)
C(1)–C(17)	1.531 (5)	C(9)–C(10)	1.394 (6)
C(2)–C(3)	1.542 (6)	C(10)–C(11)	1.436 (5)
C(3)–C(4)	1.535 (5)	C(10)–C(15)	1.424 (5)
C(3)–C(16)	1.518 (5)	C(11)–C(12)	1.331 (6)
C(3)–C(20)	1.528 (6)	C(12)–C(13)	1.367 (7)
C(4)–C(5)	1.542 (6)	C(13)–C(14)	1.371 (6)
C(5)–C(6)	1.546 (5)	C(14)–C(15)	1.406 (6)
C(5)–C(18)	1.542 (5)	C(15)–C(16)	1.409 (5)
C(5)–C(19)	1.513 (6)		

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Dichlorobis(pyridine)zinc(II) – a Redetermination

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Abstract. Dichlorobispyridinezinc(II), $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Cl}_2\text{Zn}$, *M.W.* 294.50, monoclinic, $P2_1/c$, $a = 8.580$ (3), $b = 17.677$ (11), $c = 8.397$ (5) Å, $\beta = 101.42$ (4)°; $V = 1248.4$ (1.2) Å³; $d_m = 1.56$, $d_c = 1.567$ g cm^{–3} for $Z = 4$. The final *R* was 0.047 for the 1266 reflections used in

the analysis. The Zn atom is in the center of an approximately tetrahedral arrangement of the two Cl atoms [Zn–Cl is 2.215 (2) and 2.228 (2) Å] and the two N atoms [Zn–N is 2.046 (5) and 2.052 (6) Å] from the pyridine rings. The pyridine rings pack in two differ-

ent ways; one type forms dimer-like pairs related by a center of symmetry, and the second ring packs in an infinite chain generated by the *c* glide.

Introduction. Crystals of ZnCl_2py_2 , py is pyridine, were obtained by slowly evaporating an ethanol solution of ZnCl_2 and py (in a 1:2 mole ratio). Preliminary Weissenberg and precession photographs indicated the probable space group to be $P2_1/c$. A crystal $0.47 \times 0.33 \times 0.17$ mm was mounted on a glass fiber and was used for all subsequent measurements. The experimental details are similar to those given by Dymock & Palenik (1974). The intensity data were measured using graphite-monochromatized Mo $K\alpha$ radiation to a 2θ limit of 45° . Of the 1638 reflections measured, those 1266 re-

flections with $I \geq 2.0\sigma(I)$ were considered reliable and were used in the analysis. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by the application of Lorentz-polarization corrections. The monochromator was assumed to be a 50% perfect and 50% mosaic crystal.

The heavy-atom method was employed together with Fourier syntheses. Refinement was carried out by least-squares techniques using first isotropic and then anisotropic thermal parameters. The positions of the H atoms were determined from a difference Fourier synthesis and were included in subsequent structure-factor calculations but their parameters were not varied. The final R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.047 for the 1266 reflections used in the analysis. The final parameters for the non-hydrogen atoms are given in Table 1 and for the hydrogen atoms in Table 2.* The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$, where $w = F_o^2/a^2$ if $|F_o| < a$, $w = 1$ if $a \leq |F_o| \leq b$, and $w = b^2/F_o^2$ if $|F_o| > b$, where $a = 25.0$ and $b = 50.0$. The scattering factors for Zn, Cl, N, and C were taken from Hanson, Herman, Lea & Skillman (1964) and for H from Stewart, Davidson & Simpson (1965).

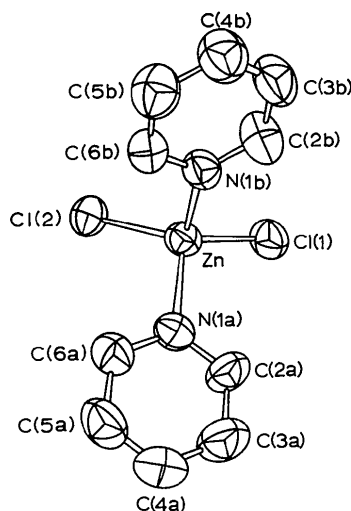


Fig. 1. An ORTEP drawing of the ZnCl_2py_2 molecule showing the thermal ellipsoids and atomic numbering. Pertinent distances are Zn-Cl(1) of 2.215 (2), Zn-Cl(2) of 2.228 (2), Zn-N(1a) of 2.046 (5) and Zn-N(1b) of 2.052 (6) Å. The angles in the coordination sphere are Cl(1)-Zn-Cl(2) of 120.9 (1), Cl(1)-Zn-N(1a) of 108.1 (2), Cl(1)-Zn-N(1b) of 107.1 (2), Cl(2)-Zn-N(1a) of 107.1 (2), Cl(2)-Zn-N(1b) of 106.4 (2) and N(1a)-Zn-N(1b) of 106.3 (2)°.

Discussion. A series of dichlorobis(4-substituted pyridine)zinc(II) complexes was being studied in our laboratory and we wished to compare the Zn-Cl and Zn-N distances with those in the pyridine complex. Therefore, we undertook a redetermination of the ZnCl_2py_2 structure since the data reported by Sokolova, Atovmyan & Porai-Koshits (1965), henceforth SAP, were poorly refined (R was 16%). An ORTEP drawing of ZnCl_2py_2 showing the atomic numbering and thermal ellipsoids determined from our study is shown in Fig. 1.

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31332 (10 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. The final parameters of non-hydrogen atoms in $\text{ZnCl}_2(\text{py})_2$

All values are $\times 10^4$, except those for Zn, which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	76885 (9)	11769 (5)	20659 (9)	1366 (12)	368 (3)	1449 (13)	-8 (12)	759 (18)	-28 (12)
Cl(1)	6503 (2)	196 (1)	2959 (2)	203 (4)	41 (1)	223 (4)	-11 (3)	156 (6)	25 (3)
Cl(2)	9820 (2)	1710 (1)	3604 (2)	159 (3)	51 (1)	188 (3)	-15 (3)	10 (5)	-24 (3)
N(1a)	8304 (6)	876 (3)	-81 (6)	166 (9)	42 (2)	153 (9)	13 (8)	98 (16)	13 (8)
C(2a)	7596 (11)	319 (4)	-968 (9)	279 (20)	49 (3)	177 (13)	-62 (14)	132 (25)	-44 (11)
C(3a)	8016 (13)	92 (6)	-2390 (10)	341 (23)	60 (4)	204 (16)	-42 (17)	171 (30)	-52 (14)
C(4a)	9191 (11)	468 (6)	-2916 (10)	261 (18)	64 (4)	185 (15)	82 (15)	163 (27)	2 (13)
C(5a)	9934 (11)	1041 (6)	-2003 (11)	254 (18)	84 (5)	233 (17)	-39 (15)	224 (28)	8 (15)
C(6a)	9456 (10)	1250 (6)	-587 (9)	228 (15)	60 (5)	206 (13)	-60 (15)	177 (23)	-27 (14)
N(1b)	6015 (7)	2016 (3)	1517 (6)	126 (10)	40 (2)	166 (9)	-8 (8)	54 (15)	-2 (8)
C(2b)	4511 (10)	1902 (6)	1652 (10)	155 (14)	55 (5)	293 (16)	-9 (13)	80 (23)	61 (14)
C(3b)	3407 (10)	2484 (6)	1435 (13)	153 (16)	51 (4)	404 (22)	18 (13)	126 (29)	38 (16)
C(4b)	3820 (10)	3183 (5)	1049 (11)	171 (15)	54 (4)	297 (20)	16 (12)	75 (26)	29 (14)
C(5b)	5369 (10)	3303 (4)	916 (9)	222 (17)	39 (3)	256 (15)	-1 (12)	32 (24)	31 (11)
C(6b)	6437 (8)	2712 (4)	1142 (8)	161 (12)	44 (3)	195 (12)	-29 (10)	67 (19)	10 (10)

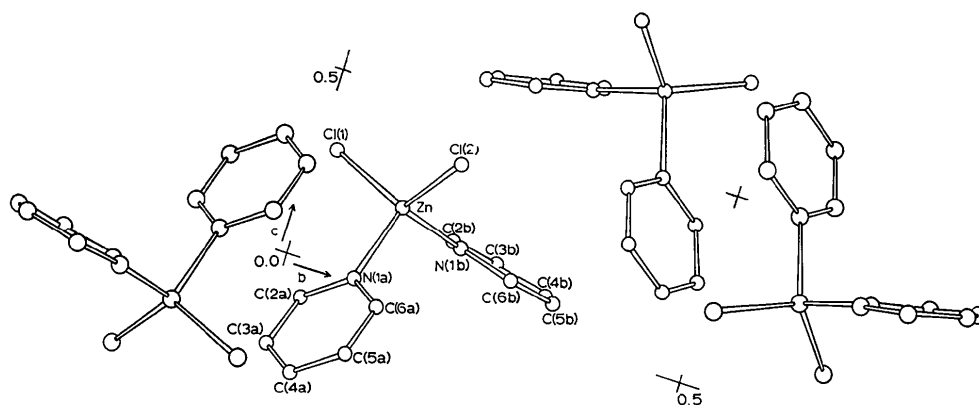


Fig. 2. A packing diagram viewed approximately down c illustrating the two different stacking arrangements of the pyridine rings. The pyridine ring N(1a) to C(6a) is the 'a-ring' or type II and the N(1b) to C(6b) is the 'b-ring' or type I.

Table 2. The final parameters of the hydrogen atoms in $\text{ZnCl}_2(\text{py})_2$

The positional parameters are $\times 10^3$. The number in parentheses is the number of the C atom to which the H is bonded at a distance given in the last column.

	x	y	z	B (\AA^2)	Distance (\AA)
H(2a)	707	-22	-66	7.2	1.11
H(3a)	743	-56	-299	8.2	1.32
H(4a)	987	23	-382	6.7	1.12
H(5a)	1089	142	-193	7.5	1.05
H(6a)	1006	181	8	7.2	1.21
H(2b)	403	146	251	7.6	1.19
H(3b)	206	240	171	7.9	1.23
H(4b)	295	380	88	7.4	1.31
H(5b)	556	385	41	6.7	1.08
H(6b)	784	282	126	5.9	1.20

The Zn-N distances [Zn-N(1) is 2.046 (5) and Zn-N(2) is 2.052 (6) \AA] average 2.049 \AA and are slightly longer than the average of 2.01 \AA reported by SAP, and the values of 2.044 \AA found in $\text{ZnCl}_2(4\text{-CH}_3\text{-py})_2$ by Lynton & Sears (1971), henceforth LS. While the difference between 2.049 and 2.044 \AA is not significant, the shorter distances for the 4- CH_3 -py derivative are reasonable in terms of the relative pK_b 's given by Perrin (1975) of 8.77 for py and 8.00 for 4- CH_3 -py. A more complete discussion of the variation in the Zn-N distances versus pK_b will be deferred until our other studies have been completed.

The Zn-Cl distances of 2.215 (2) and 2.228 (2) \AA appear to be significantly different and are slightly longer than the original values of SAP of 2.18 \AA and the values of 2.204 (2) and 2.211 (2) reported by LS for the 4- CH_3 -py complex. The small but significant lengthening of the Zn-Cl distances in the pyridine derivative is probably due to the non-bonded interactions between the Cl atoms and the H atoms on the pyridine rings. There are short Cl...H contacts both intramolecularly and intermolecularly with the latter related to the packing of the pyridine rings (see below).

The various angles in the coordination sphere deviate

from ideality in a manner which reflects the various non-bonded contacts. The Cl-Zn-Cl angle of 120.9 (1) $^\circ$ is very large to minimize Cl...Cl interactions. In the corresponding 4- CH_3 -py complex, where LS found the Zn-Cl distances were slightly smaller, the Cl-Zn-Cl angle opens up to 121.8 (1) $^\circ$. The N-Zn-N angles of 106.3 (2) in the py derivative and 100.6 (2) $^\circ$ in the 4- CH_3 -py complex reflect the larger Cl-Zn-Cl angle.

A final point of interest concerns the packing in the crystal which is somewhat unique for the pyridine complex because the 4 position has only the relatively small H atom. As noted by SAP there are two types of stacking in the ZnCl_2py_2 crystal, see Fig. 2. The 'a' rings or type II of SAP are related by a center of symmetry into dimer-like units. The rings are parallel and about 3.7 \AA apart. The 'b' rings or the type I of SAP are related by the c glide and form an infinite column in the crystal. The rings are tipped about 25 $^\circ$ from being parallel, and the interplanar distances vary from 3.4 to 4.1 \AA .

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