

six-membered ring is in a chair form. The bond lengths other than C(1)—C(10) are shorter [especially C(11)—C(12), 1.496 (4), and C(12)—C(13), 1.506 (4) Å] than the standard value. The five-membered ring is in a half-chair form, C(1), C(15), C(16) and O being approximately in a plane. It can be concluded that the deformation of these rings has resulted from the minimization of steric repulsions between adjacent H atoms in the same ring and those between adjacent H atoms in different rings. This is clearly seen in Fig. 2.

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Dibromo(*N*-tetrakis-4-pyridinecarbaldehyde)cobalt(II)

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Abstract. $\text{CoBr}_2(\text{OHC}_5\text{H}_4\text{N})_4$, tetragonal, $P4nc$, $a = b = 11.713$ (4), $c = 9.277$ (5) Å, $U = 1272.8$ Å³, $Z = 2$, $D_x = 1.69$ g cm⁻³. The structure was solved by Patterson methods and refined to an R of 0.049 for 328 unique diffractometer data. The Co and Br atoms lie on the fourfold molecular symmetry axis; the ligands are coordinated through their N atoms which complete the octahedral coordination of Co.

Introduction. The enzyme alcohol dehydrogenase catalyses the reduction of acetaldehyde by the cofactor nicotinamide adenine dinucleotide (NADH) and *in vitro* will catalyse the reduction of pyridinecarbaldehydes to the carbinols. Hughes & Prince (1977) have performed a kinetic study of this reaction and of the metal-catalysed reduction of pyridinecarbaldehydes by *N*-benzylidihydronicotinamide, an analogue of NADH. The mode of coordination of metals by pyridinecarbaldehydes is important in the interpretation of these experiments (Hughes, Prince & Wyeth, 1977).

The sample was obtained as red tetragonal parallelepipeds from the reaction between solutions of cobalt(II) bromide (0.05 *M*) and 4-pyridinecarbaldehyde (1.0 *M*) in anhydrous acetonitrile. 1890 reflexions were measured with a Syntex $P2_1$ four-circle diffractometer, $\text{Mo } K\alpha$ radiation, a graphite mono-

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chromator and a crystal $0.23 \times 0.24 \times 0.34$ mm. After application of L_p and numerical absorption corrections [$\mu(\text{Mo } K\alpha) = 37.44$ cm⁻¹], equivalent reflexions were averaged to give 328 unique reflexions with $|F| > 4\sigma(F)$ based on counting statistics.

The Co and Br atoms, which lie on special positions (0, 0, z), were located by Patterson methods, and the remaining atoms (except H) located by difference syntheses. The structure was refined by blocked cascade least squares with H atoms constrained to lie 1.08 Å from C on the external bisectors of the angles at C. An overall H-atom isotropic temperature factor was employed, with individual anisotropic factors for the remaining atoms. Complex neutral-atom scattering factors were used, and the weighting scheme was $w = 1/\sigma^2(F)$. The refinement converged to $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.0297$, $R = 0.0488$. The enantiomorphous structure refined to 0.0310 and 0.0502 respectively, and so was rejected. Final atomic coordinates and thermal parameters are given in Tables 1–3 and the resulting bond lengths and angles in Tables 4–5.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31992 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom coordinates* ($\times 10^4$)

	x	y	z
Co	0	0	0
Br(1)	0	0	2705 (6)
Br(2)	0	0	-2897 (6)
N	700 (6)	1736 (5)	-88 (14)
C(1)	1592 (8)	2039 (8)	690 (13)
C(2)	2145 (9)	3106 (10)	518 (14)
C(3)	1702 (9)	3851 (8)	-483 (14)
C(4)	747 (10)	3581 (8)	-1245 (16)
C(5)	288 (8)	2484 (8)	-1010 (13)
C(6)	2258 (11)	5003 (11)	-704 (13)
O	1901 (8)	5695 (7)	-1489 (14)

Table 2. *Anisotropic temperature factors* ($\text{\AA}^2 \times 10^3$)

The temperature factor exponent takes the form:
 $-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	38 (1)	38 (1)	52 (2)	0	0	0
Br(1)	61 (2)	61 (2)	54 (2)	0	0	0
Br(2)	48 (2)	48 (2)	47 (2)	0	0	0
N	38 (4)	34 (4)	55 (5)	-7 (10)	1 (11)	3 (4)
C(1)	37 (7)	40 (7)	62 (7)	-3 (6)	-6 (6)	4 (6)
C(2)	39 (8)	56 (8)	71 (10)	-1 (8)	8 (7)	-2 (7)
C(3)	27 (6)	34 (6)	62 (10)	-12 (6)	28 (6)	-5 (5)
C(4)	45 (7)	44 (7)	69 (7)	2 (8)	6 (8)	2 (5)
C(5)	25 (8)	37 (6)	60 (7)	-6 (5)	2 (5)	3 (5)
C(6)	50 (7)	37 (6)	125 (15)	-38 (15)	10 (6)	-18 (11)
O	62 (6)	50 (6)	166 (11)	20 (7)	21 (7)	8 (4)

Table 3. *Hydrogen atom coordinates* ($\times 10^4$) and *isotropic temperature factors* ($\text{\AA}^2 \times 10^3$)

The U value for each H atom is 0.081 (16) \AA^2 .

	x	y	z
H(1)	1909	1439	1479
H(2)	2877	3339	1162
H(4)	352	4193	-1958
H(5)	-463	2266	-1628
H(6)	3011	5204	-81

Table 4. *Bond lengths* (\AA)

Co—Br(1)	2.509 (9)	Co—Br(2)	2.688 (9)
Co—N	2.194 (8)	N—C(1)	1.319 (15)
N—C(5)	1.316 (15)	C(1)—C(2)	1.417 (16)
C(2)—C(3)	1.376 (18)	C(3)—C(4)	1.360 (18)
C(4)—C(5)	1.409 (15)	C(3)—C(6)	1.512 (18)
C(6)—O	1.167 (17)		

Discussion. The complex (Fig. 1) possesses a four-fold crystallographic symmetry axis along the Br(1)—Co—Br(2) bonds. Co—Br(2) [2.688 (9) \AA] is appreciably longer than Co—Br(1) [2.509 (9) \AA], and this is associated with a significant distortion of the octa-

Table 5. *Bond angles* ($^\circ$)

Br(1)—Co—Br(2)	180.0	Br(1)—Co—N	92.1 (4)
Br(2)—Co—N	87.9 (4)	N—Co—N'	89.9 (1)
Co—N—C(1)	121.7 (8)	Co—N—C(5)	120.3 (8)
C(1)—N—C(5)	117.9 (9)	N—C(1)—C(2)	122.6 (11)
C(1)—C(2)—C(3)	117.6 (11)	C(2)—C(3)—C(4)	120.9 (11)
C(2)—C(3)—C(6)	119.6 (11)	C(4)—C(3)—C(6)	119.4 (11)
C(3)—C(4)—C(5)	116.5 (11)	N—C(5)—C(4)	124.5 (11)
C(3)—C(6)—O	123.3 (12)		

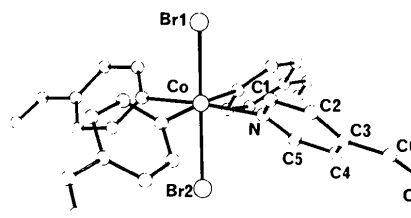


Fig. 1. One molecule of the complex, showing the labelling of the unique atoms.

hedral coordination towards square pyramidal with Br(2) excluded [Br(1)—Co—N 92.1(4) $^\circ$, Br(2)—Co—N 87.9(4) $^\circ$].

The pyridine rings are tilted by 44 $^\circ$ to the equatorial plane. The Co—N distance of 2.194 (8) \AA is longer than most Co—N bonds, but similar to the values in bis(1,5-diphenyl-1,3,5-pentanetrionato)tetrapyridinecobalt(II)—tetrapyridine (Kuszaj, Tomlonovic, Murtha, Lintvedt & Glick, 1973) and in bis(2,4-pentanedionato)cyclohexylaminecobalt(II) (Bertrand & Kalyanaraman, 1971).

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