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Tetraaquabis[5-(4-pyridyl *N*-oxide)-tetrazolato-κN^2]cadmium: the intermediate in the synthesis of a tetrazole from a nitrile and an azide

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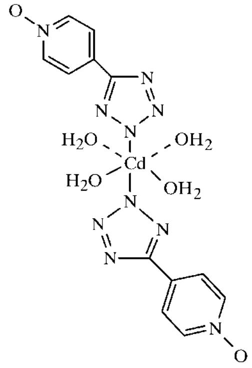
The intermediate [Cd(4-PTZ)$_2$(H$_2$O)$_4$] [4-PTZ is 5-(4-pyridyl *N*-oxide)tetrazolate, $C_6H_4N_5O$], (I), in the synthesis of 4-HPTZ, (II), from the cycloaddition reaction of 4-cyanopyridine *N*-oxide with NaN_3 in water using $CdCl_2$ as catalyst, was structurally characterized. The unique Cd atom lies on a twofold axis and the coordination geometry of the Cd atom is that of a slightly distorted octahedron, involving four water molecules and two tetrazolate ligands. The catalytic role of the Cd^{2+} ion in the tetrazole generation reaction stems from the formation of (I). In acidic solution, (I) can be disassociated and the free ligand, (II), can be released.

Comment

Tetrazoles provide an increasingly popular type of functional group (Butler, 1996) which has applications in coordination chemistry as a ligand (Franke & Groeneveld, 1980; Erbe & Beck, 1983; Kreutzer *et al.*, 1983), in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group (Singh *et al.*, 1980) and in various materials sciences, including specialty explosives (Ostrovskii *et al.*, 1999). It has long been known that simple heating of azide salts with a nitrile in solution produces the corresponding tetrazole (Dimroth & Fester, 1910). Demko & Sharpless (2001) have recently modified this transformation and developed an environmentally friendly, relatively simple, route. In this general reaction, tetrazoles are prepared by the addition of azides to nitriles in water, with the catalysis of Lewis acids such as zinc salts. However, the intermediate was not characterized, and thus the catalytic mechanism of the Lewis acid is unknown. Although Xiong and co-workers (Wang *et al.*, 2003; Xiong *et al.*, 2002; Xue, Abrahams *et al.*, 2002; Xue, Wang *et al.*, 2002) have recently tried to isolate and characterize these intermediates, the exact intermediate is still unknown, because potentially bridging substituted nitriles were used in these experiments and a series of complicated tetrazole coordination polymers were formed. A structural investigation of this intermediate would be very interesting because it may provide important clues to the role of the Lewis acid in the tetrazole synthesis reaction, which in turn may allow synthetic chemists to optimize this synthetic approach further. In order to obtain a high-quality crystalline material for X-ray structural analysis, we chose to use a water-soluble nitrile (4-cyanopyridine *N*-oxide). In addition, the selected nitrile has a strong electron-withdrawing group, which can accelerate the cycloaddition reaction to form the tetrazole (Demko & Sharpless, 2001). We report here the X-ray structure of the intermediate [Cd(4-PTZ)$_2$(H$_2$O)$_4$] [4-PTZ is 5-(4-pyridyl *N*-oxide)tetrazolate], (I), in the formation of 4-HPTZ, (II), from the reaction of 4-cyanopyridine *N*-oxide with NaN_3 using $CdCl_2$ as catalyst.



(I)

A crystallographic twofold axis passes through the Cd atom in the molecule of (I), relating the two equal parts of the molecule (Fig. 1). The coordination geometry of the Cd atom is that of a slightly distorted octahedron, involving four water molecules and two tetrazolate ligands. The O atoms of the four water molecules form a square-planar arrangement around the Cd center, and the tetrazolate ligands coordinate to the Cd atom *via* atom N1. The dipolar cycloaddition of azides with nitriles can lead to two isomers, *i.e.* a 4-*R* or a 5-*R* coordinated ligand may be formed (see scheme below). In (I), as observed in the indium tetrazolate complex (Guilard *et al.*, 1987), only the 4-*R* tetrazolate is formed, because it has a sterically favorable configuration. The coordinated tetrazole ring takes the form of a planar pentagon, with bond lengths [1.317 (2)–1.339 (2) Å; Table 1] intermediate between those of single and double bonds. The dihedral angle between the tetrazolate plane and the C1-bonded 4-pyridyl ring is only 18.5 (2)°, favoring an orbital conjugation between the two cycles. The molecules are packed in such a way that intermolecular O—H···O hydrogen-bonding interactions [2.670 (2), 2.756 (2) and 2.764 (2) Å] between the coordinated water and the pyridyl *N*-oxide O atom, and an intermolecular O—H···N hydrogen bond [2.847 (2) Å] between the coordinated water and a tetrazole N atom result in an infinite three-dimensional structure. There is a significant π–π stacking interaction along the *b* direction between the tetrazole ring and the neighbouring 4-pyridyl rings, with a centroid–centroid separation of

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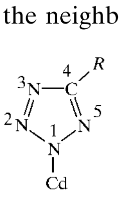
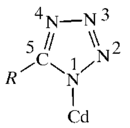
3.57 Å and a perpendicular distance of 3.38 Å; additionally, the 4-pyridyl ring in the same unit also has the same π–π interaction with the neighbouring tetrazole rings.



4-*R* isomer



5-*R* isomer

With the elucidation of the structure of the intermediate, we can state that the catalytic mechanism exhibited by Lewis acids in the synthesis of tetrazoles from the reaction of nitriles with azides stems from the formation of metal–tetrazolate complexes. With the disassociation of the complex in acidic media, the tetrazole can be released.

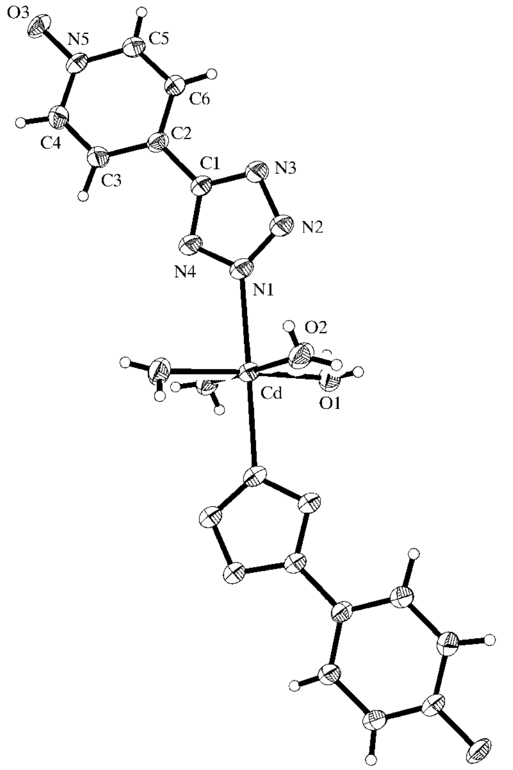


Figure 1
A view of (I), showing the atom-labeling scheme and 50% probability displacement ellipsoids.

Experimental

A solution of 4-cyanopyridine *N*-oxide (0.060 g, 0.5 mmol) in distilled water (30 ml), and a solution of sodium azide (0.033 g, 0.5 mmol) and cadmium chloride (0.050 0.3 mmol) in water (10 ml) were mixed and allowed to stand at room temperature for a few days. The resulting cycloaddition reaction produced the tetrazole ligand *in situ*, and white block-like crystals of (I) (0.103 g, 81% yield) were obtained after washing thoroughly with distilled water and methanol. Analysis calculated for $C_{12}H_{16}CdN_{10}O_6$: C 28.23, H 3.16, N 27.46%; found: C 28.01, H 3.45, N 27.19%. The free tetrazole, (II), was obtained by dissolving (I) in 2 *N* HCl solution, followed by extraction with ethyl acetate and evaporation of the organic layer. ^{1}H NMR (DMSO-d_6): δ 8.17 (*d*, 2H, J = 6.7 Hz), 7.98 (*d*, 2H, J = 6.7 Hz). Analysis calculated for $C_6H_5N_5O$: C 44.16, H 3.09, N 42.94%; found: C 44.38, H 3.42, N 42.62%.

Crystal data

$[Cd(C_6H_4N_5O)_2(H_2O)_4]$
$M_r = 508.75$
Monoclinic, $C2/c$
$a = 21.871$ (4) Å
$b = 7.0825$ (14) Å
$c = 11.417$ (2) Å
$\beta = 96.52$ (3)°
$V = 1757.2$ (6) Å^3
$Z = 4$
$D_x = 1.923$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 672 reflections
$\theta = 3.0$–30.0°
$\mu = 1.30$ mm^{-1}
$T = 223$ (2) K
Polyhedron, white
0.30 × 0.15 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995, 1997)
$T_{\min} = 0.793$, $T_{\max} = 0.880$
12 672 measured reflections
2519 independent reflections
2338 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 30.0°$
$h = -30 \rightarrow 29$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$
4200 standard reflections every 250 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.066$
$S = 1.05$
2519 reflections
148 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.2051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—N1	2.2938 (17)	N4—C1	1.330 (2)
Cd—O1	2.2945 (15)	N5—C5	1.342 (2)
Cd—O2	2.2948 (15)	N5—C4	1.347 (2)
O3—N5	1.3317 (19)	C1—C2	1.459 (2)
N1—N2	1.317 (2)	C2—C3	1.385 (3)
N1—N4	1.334 (2)	C2—C6	1.389 (2)
N2—N3	1.332 (2)	C3—C4	1.373 (3)
N3—C1	1.339 (2)	C5—C6	1.373 (3)
O1—Cd—O1$^{\rm i}$	77.17 (9)	O1—Cd—O2	98.90 (6)
O1—Cd—O2$^{\rm i}$	175.23 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···N2$^{\rm ii}$	0.80 (3)	2.05 (3)	2.847 (2)	169.46 (4)
O2—H2B···O3$^{\rm iii}$	0.74 (3)	2.02 (3)	2.764 (2)	173.52 (4)
O1—H1A···O3$^{\rm iv}$	0.76 (3)	1.92 (3)	2.670 (2)	175.27 (4)
O1—H1B···O3$^{\rm v}$	0.78 (3)	1.98 (3)	2.756 (2)	171.70 (4)

Symmetry codes: (ii) $1 - x, -y, 1 - z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Water H atoms were located in difference maps and their parameters were refined isotropically [O—H = 0.74 (3)–0.80 (3) Å]. All other H atoms were positioned geometrically and treated as riding, with C—H distances of 0.94 Å and $U_{\rm iso}$(H) values of 1.2$U_{\rm eq}$(C).

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *maXus* (Mackay *et al.*, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1236). Services for accessing these data are described at the back of the journal.

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