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Metal–nucleobase interaction: dibromobis(cytosine)-cadmium(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.061
wR factor = 0.158
Data-to-parameter ratio = 18.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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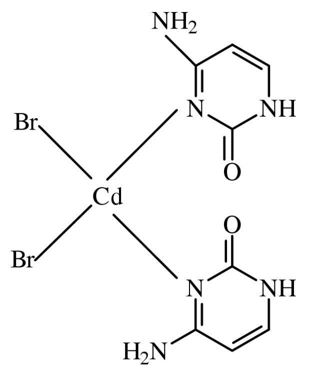
In the crystal structure of the title compound, [$CdBr_2$-($C_4H_5N_3O)_2$], two N atoms at the 3-position of the cytosine ligands and the two bromide ions complete the distorted tetrahedral geometry around the Cd^{II} atom. The cytosine ligands of one type are paired through N—H···O hydrogen bonds while the cytosine ligands of another type are chained through N—H···O hydrogen bonds.

Comment

Studies of metal ion–nucleic acid interactions are of great current interest since metal ions play a crucial role in the structure and function of nucleic acid and genetic information transfer (Salam & Aoki, 2000). Cadmium is a metal of environmental importance since it is toxic and present in the environment as an industrial pollutant. In this paper, the interaction between cadmium(II) and cytosine, a major nucleobase, is presented. Cytosine offers many metal binding modes: *via* N3 (Tran Qui & Bagieu, 1990), through N4 (Muller *et al.*, 1998), bridging through N3 and N4 (Wienkotter *et al.*, 1995), *via* O2 only (Cervantes *et al.*, 1990), with chelation by N3 and O2 (Aoki & Saenger, 1984), and bridging through N3 and O2 (Lippert *et al.*, 1984) *via* stronger N3 with additional weaker O2 interactions (Palaniandavar *et al.*, 1996). In the title complex, (I), cytosine binds in the last mode listed above.



(I)

The Cd1 atom is coordinated by two crystallographically independent cytosine molecules (cytosine ligands *A* and *B*; atoms are labelled with a prime in *B*) through the N3, N3′ atoms of the cytosine rings. In addition to the N atoms, two bromide ions are coordinated to cadmium(II) to complete the distorted tetrahedral environment. A displacement-ellipsoid plot of the complex with the atom-labelling scheme is shown in Fig. 1. The bond lengths and angles do not differ significantly

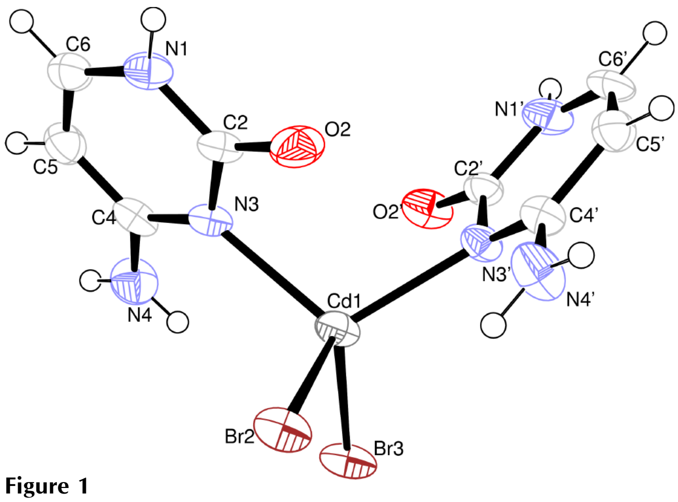


Figure 1
An *ORTEP*A view of (I) with displacement ellipsoids at the 50% probability level.

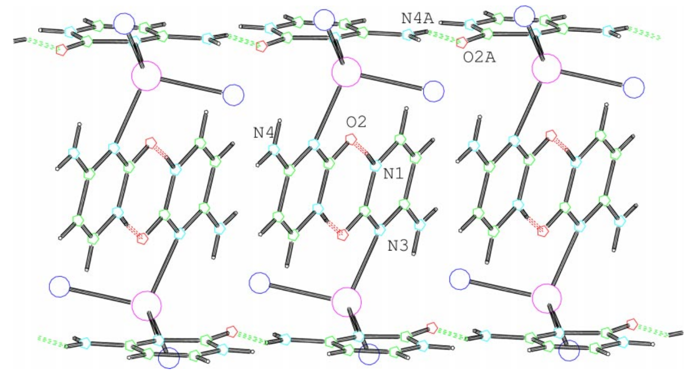


Figure 2
A view of the packing diagram of (I) showing chaining and pairing.

between the two ligands. The Cd—N(cytosine) distances are in agreement with the range of values [2.253 (2)–2.296 (3) Å] reported for cadmium chloride–cytosine complexes (Munno *et al.*, 1993; Gagnon *et al.*, 1979). The Cd—Br distances are somewhat shorter than the value of 2.747 (6) Å reported in the crystal structure of dibromobis(trimethoprim)cadmium(II) (Muthiah & Robert, 1999). In addition to the tetrahedral coordination of cadmium, there are weak Cd···O2 interactions [Cd···O2 2.824 (2) and Cd···O2′ 2.779 (4) Å], typical in metal complexes of cytosine (Palaniandavar *et al.*, 1996; Munno *et al.*, 1993). Weak Cd···O interactions [2.780 (6) and 2.677 (4) Å] have also been observed in the crystal structure of dichlorobis(1-methylcytosine)cadmium(II) (Gagnon *et al.*, 1979). There is considerable asymmetry in the exocyclic bond angles at N3 and N3′ to which cadmium is bonded. The external angles at N3 in ligand *A* are Cd—N3—C4 136.2 (5)° and Cd—N3—C2 103.8 (5)°. The corresponding angles in ligand *B* are 131.1 (5) and 105.5 (4)°, respectively, implying a definite attraction of atoms O2 and O2′ of the cytosine towards the cadmium ion.

The coordination of the metal ion does not alter the bond lengths and angles of cytosine significantly. The two cytosine planes in the cadmium complex make a dihedral angle of 79.4 (3)° with one another. The corresponding angle in dichlorobis(cytosine)cobalt(II) (Tran Qui & Bagieu, 1990) is 98.6°. Both these complexes have distorted tetrahedral geometry, whereas dichlorobis(cytosine)copper(II) (Sundara lingam & Carrabine, 1971) has a square-planar geometry and the dihedral angle between the two cytosine planes is only 7.3°.

In this cadmium complex, the crystal structure is governed by a number of intermolecular hydrogen bonds (Table 2). Of the two independent cytosine ligands, the *A* type (related by $1-x$, $1-y$, $1-z$) are paired *via* N—H···O hydrogen bonds [N1—H1···O2 2.758 (8) Å] while the *B* type form a supramolecular chain through N—H···O hydrogen bonds [N4′—H42′···O2′ 2.983 (9) Å]. This chaining and pairing are shown in Fig. 2. This type of chaining of cytosine has also been observed in 5-fluorocytosinium salicylate (Prabakaran *et al.*, 2001) and *trans*-dichloroammine(1-methylcytosine-N^3)platihydrate (Lippert *et al.*, 1981). The other H atom of the 4-amino group is involved in an interligand hydrogen bond with one of the bromide ions [N4′—H41′···Br2 3.699 (8) Å]. Such interligand hydrogen bonding confers additional stability on the coordination and plays an important role in metal–nucleic acid recognition. This type of interligand hydrogen bond has also been observed in the cadmium complex of methylcytosine (Gagnon *et al.*, 1979).

Experimental

Cytosine and cadmium bromide in a 1:1 molar ratio were dissolved in hot methanol and the resultant solution was heated over a water bath for an hour. On cooling the solution slowly, transparent colourless crystals of (I) were obtained.

Crystal data

$[CdBr_2(C_4H_5N_3O)_2]$
$M_r = 494.43$
Triclinic, $P\bar{1}$
$a = 7.874$ (2) Å
$b = 12.624$ (3) Å
$c = 7.117$ (3) Å
$\alpha = 105.87$ (4)°
$\beta = 92.67$ (3)°
$\gamma = 87.93$ (3)°
$V = 679.5$ (4) Å^3
$Z = 2$
$D_x = 2.417$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.0$–27.7°
$\mu = 7.49$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.28 × 0.23 × 0.19 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.108$, $T_{max} = 0.215$
3301 measured reflections
3301 independent reflections
2427 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.7°$
$h = -10 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 4$
1 standard reflection every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.158$
$S = 0.96$
3301 reflections
175 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1171P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.66$ e Å^{-3}
$\Delta\rho_{min} = -2.87$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—Br2	2.5920 (14)	N1′—C2′	1.348 (9)
Cd1—Br3	2.5815 (15)	N1′—C6′	1.359 (11)
Cd1—N3	2.281 (6)	N3—C2	1.368 (9)
Cd1—N3′	2.243 (6)	N3—C4	1.330 (10)
O2—C2	1.230 (10)	N3′—C2′	1.372 (9)
O2′—C2′	1.238 (9)	N3′—C4′	1.339 (9)
N1—C2	1.367 (10)	N4—C4	1.324 (10)
N1—C6	1.350 (10)	N4′—C4′	1.312 (10)
Br2—Cd1—Br3	104.24 (5)	O2—C2—N1	121.7 (7)
Br2—Cd1—N3	101.91 (15)	O2—C2—N3	119.9 (7)
Br2—Cd1—N3′	111.93 (15)	N1—C2—N3	118.4 (6)
Br3—Cd1—N3	115.59 (15)	O2′—C2′—N1′	121.8 (6)
Br3—Cd1—N3′	113.24 (16)	O2′—C2′—N3′	119.7 (6)
N3—Cd1—N3′	109.3 (2)	N1′—C2′—N3′	118.5 (6)
C2—N1—C6	121.9 (6)	N3—C4—N4	117.3 (7)
C2′—N1′—C6′	122.1 (6)	N3—C4—C5	121.3 (7)
Cd1—N3—C2	103.8 (5)	N4—C4—C5	121.4 (7)
Cd1—N3—C4	136.2 (5)	N3′—C4′—N4′	118.3 (7)
C2—N3—C4	119.8 (6)	N3′—C4′—C5′	121.5 (6)
Cd1—N3′—C2′	105.5 (4)	N4′—C4′—C5′	120.2 (7)
Cd1—N3′—C4′	131.1 (5)	N1—C6—C5	120.0 (7)
C2′—N3′—C4′	119.8 (6)	N1′—C6′—C5′	121.3 (7)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2^{i}	0.86	1.911	2.758 (8)	168
N1′—H1′$\cdots$Br3^{ii}	0.86	2.679	3.487 (7)	157
N4′—H41′$\cdots$Br2	0.86	2.895	3.699 (8)	156
N4′—H42′$\cdots$O2′^{iii}	0.86	2.155	2.983 (9)	162
C6—H6$\cdots$O2′^{iv}	0.93	2.474	3.294 (10)	147

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $x, y, 1+z$; (iv) $1-x, 1-y, -z$.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1997); software used to prepare material for publication: *PLATON*.

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