C(3)	0.0400 (6)	0.5867 (5)	0.2055 (8)	4.5 (2)
C(4)	0.1324 (6)	0.5343 (5)	0.3181 (9)	5.1 (2)
C(5)	0.1082 (5)	0.4858 (6)	0.407 (1)	6.6 (2)
C(6)	0.194 (1)	0.4308 (7)	0.507 (1)	8.0 (3)
C(7)	0.303 (1)	0.4238 (7)	0.523 (1)	7.8 (3)
C(8)	0.3303 (8)	0.4703 (7)	0.437 (1)	8.0 (3)
C(9)	0.2453 (7)	0.5253 (6)	0.333 (1)	6.4 (2)
C(10)	0.0530 (6)	0.7092 (5)	−0.2524 (8)	5.1 (2)
C(11)	0.1633 (7)	0.6856 (5)	−0.2493 (8)	5.2 (2)
C(12)	0.2299 (6)	0.6962 (5)	−0.1016 (8)	4.6 (2)
C(13)	0.3549 (6)	0.6800 (5)	−0.0420 (9)	5.2 (2)
C(14)	0.4225 (8)	0.6124 (7)	−0.118 (1)	7.3 (3)
C(15)	0.541 (1)	0.6000 (9)	−0.059 (2)	9.5 (4)
C(16)	0.5914 (9)	0.654 (1)	0.074 (1)	9.4 (4)
C(17)	0.5262 (8)	0.7230 (10)	0.154 (1)	8.1 (3)
C(18)	0.4092 (6)	0.7359 (7)	0.0943 (9)	6.0 (2)
C(19)	−0.1307 (6)	0.9573 (6)	0.0283 (10)	5.9 (2)
C(20)	−0.0924 (6)	1.0329 (5)	0.148 (1)	6.3 (2)
C(21)	0.0157 (6)	0.9871 (5)	0.2306 (8)	5.0 (2)
C(22)	0.0932 (6)	1.0343 (5)	0.3688 (8)	4.7 (2)
C(23)	0.0481 (7)	1.0994 (6)	0.4767 (9)	6.0 (2)
C(24)	0.118 (1)	1.1455 (7)	0.607 (1)	7.3 (3)
C(25)	0.232 (1)	1.1272 (8)	0.632 (1)	8.3 (3)
C(26)	0.2783 (6)	1.0633 (7)	0.527 (1)	7.7 (3)
C(27)	0.2088 (7)	1.0179 (6)	0.3956 (9)	5.8 (2)
C(28)	0.2967 (6)	0.7835 (5)	0.4716 (9)	5.0 (2)
C(29)	0.3927 (6)	0.8094 (5)	0.6032 (8)	4.9 (2)
C(30)	0.4986 (7)	0.8016 (7)	0.5928 (10)	7.0 (2)
C(31)	0.5875 (8)	0.828 (1)	0.719 (1)	9.7 (3)
C(32)	0.5727 (10)	0.8635 (9)	0.853 (1)	8.7 (3)
C(33)	0.468 (1)	0.8726 (8)	0.863 (1)	8.3 (3)
C(34)	0.3784 (7)	0.8463 (7)	0.7405 (10)	6.6 (2)
B(1)	−0.0521 (6)	0.7643 (7)	−0.0580 (10)	5.0 (2)

Table 2. *Selected geometric parameters* (Å, °)

Zn(1)—O(1)	1.935 (5)	O(2)—C(28)	1.252 (8)
Zn(1)—N(1)	2.044 (6)	C(28)—C(29)	1.463 (10)
Zn(1)—N(3)	2.084 (5)	Zn(1)···O(2)	2.534 (6)
Zn(1)—N(5)	2.038 (5)	Zn(1)···B(1)	2.985 (7)
O(1)—C(28)	1.295 (9)	O(1)···B(1)	4.901 (8)
O(1)—Zn(1)—N(1)	131.3 (2)	Zn(1)—O(1)—C(28)	103.5 (4)
O(1)—Zn(1)—N(3)	113.4 (2)	O(1)—C(28)—O(2)	120.9 (7)
O(1)—Zn(1)—N(5)	122.6 (2)	O(1)—C(28)—C(29)	116.6 (6)
N(1)—Zn(1)—N(3)	90.0 (2)	O(2)—C(28)—C(29)	122.5 (7)
N(1)—Zn(1)—N(5)	97.0 (2)	O(1)—Zn(1)···B(1)	169.5 (3)
N(3)—Zn(1)—N(5)	92.1 (2)		

The structure was solved by the direct methods (*SHELXS*86; Sheldrick, 1985) which revealed the position of the Zn atom. The remaining atoms were located by Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically by full-matrix least-squares methods, H atoms were located from a difference electron density map, placed in fixed positions (C—H = 0.95, 1.00 Å, B—H = 1.05 Å) but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Structure solution: *SHELXS*86; *DIRDIF*. Structure refinement: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Water-Bridged Molecular Adduct of Tetrabromocadmate(II) with Protonated Dafone (4,5-Diazafluoren-9-one), $(C_{11}H_7N_2O)_2[CdBr_4].2H_2O$

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Abstract

The structure of the title compound, bis(4H^+-9-oxo-4,5-diazafluorenium) tetrabromocadmate(II)–water (1/2), consists of a distorted tetrahedral $(CdBr_4)^{2-}$ anion and HL^+ cations, where L is the organic ligand dafone (4,5-diazafluoren-9-one). There is no direct bonding between the metal atom and the ligand. The protonation of one of the N atoms in the dafone ring system gives rise to an opening of the C—N—C angle when compared with the corresponding value in the neutral form. The dihedral angles between the mean planes of the pyridine

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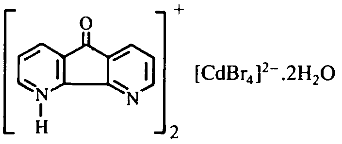
rings in each dafone ligand are 2.8 and 3.1°. The water molecules present in the structure are involved in a series of hydrogen-bonding interactions and bridge the cadmium tetrabromide and the organic ligand through weak O···Br interactions.

Comment

Studies on binuclear transition metal complexes bridged by heterocyclic aromatic diamines provide models for understanding metalloenzymes (Matsumoto, Ooi, Nakao, Mori & Nakahara, 1981). In particular, cadmium complexes have been studied, since cadmium readily replaces zinc in metalloenzymes and since the complexes can be studied by ^{113}Cd NMR spectroscopy (Hazell, 1988). The structure analysis of the title compound, (I), is a continuation of a program of structural studies of the interaction of carbonyl-bridged bipyridine with various metals (Ravikumar & Venkata Lakshmi, 1994).



(I)

The molecular structure is shown in Fig. 1. The Cd^{II} ion is surrounded by four Br$^-$ ions in a distorted tetrahedral arrangement. The average Cd—Br distance of 2.589 (8) Å is considerably longer than that of 2.506 (1) Å found in a cadmium bromide–crown ether complex (Hazell, 1988), but is shorter than that found in $CdBr_2.4H_2O$ [2.746 (4) Å] (Leligny & Monier, 1978). The spread in the Br—Cd—Br angles [103.7 (1)–117.2 (1)°] may be due, in part, to the weak hydrogen-bonding interactions between the Br atoms and the neighbouring water molecules. There is no direct bonding between the metal atom and the organic ligand.

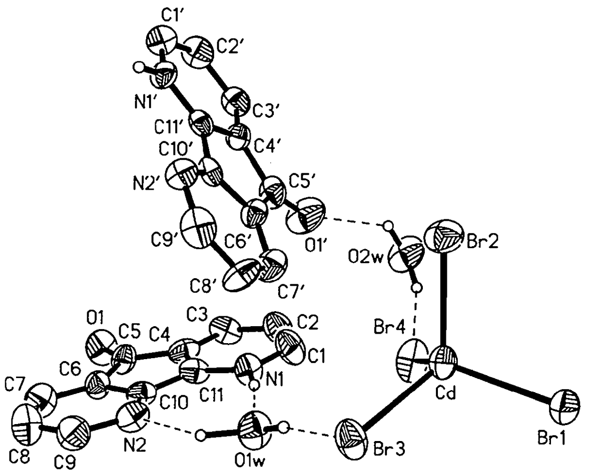


Fig. 1. Perspective view of the association, *via* N—H···O, O—H···N, O—H···O and O—H···Br (weak) hydrogen bonds, in the asymmetric unit. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. H(C) atoms have been omitted for clarity.

The two independent dafone ring systems have very similar geometries and conformations. The protonation on the N1 and N1′ atoms gives rise to an opening of the angles C1—N1—C11 [119.0 (5)°] and C1′—N1′—C11′ [119.0 (6)°], when compared with the values for the unprotonated N2 and N2′ [115.1 (5) and 113.3 (6)°, respectively], with neutral dafone itself [114.0 (3)°] and with bis(dafone) tetrachlorocobaltate(II) dihydrate [114.2 (2)°] (Ravikumar & Venkata Lakshmi, 1994). The protonated pyridine rings in both dafone molecules deviate less from planarity than the unprotonated ones. The dihedral angles between the mean planes of the pyridine rings in each dafone ligand are 2.6 (2) and 3.0 (1)°, respectively.

The water molecules are involved in a series of intermolecular hydrogen bonds (Table 3). All H atoms involved in O*w*—H or N—H bonds are hydrogen bonded to Br, N or O acceptors. The H···N distances range from 1.79 (3) to 2.59 (4) Å and the H···O distances from 1.83 (4) to 2.29 (3) Å. These values correspond to interactions of moderate to weak strength. The *D*—H···*A* angles vary from 107 (2) to 171 (3)°. The larger angles are associated with shorter H···*A* distances, as has been observed for a variety of hydrogen bonds (Hamilton & Ibers, 1968). The O*w*···Br distances of 3.372 (5) and 3.691 (4) Å are longer than the normally accepted distance of 3.28 Å for an O···Br hydrogen bond (Kuleshova & Zorkii, 1981), and so may be considered as weak interactions.

Experimental

The ligand, dafone, was prepared as described by Henderson, Fronezek & Cherry (1984). 2 mmol of dafone was dissolved in 50 ml of aqueous methanol, then 1 mmol of cadmium bromide was added to the solution along with a few drops of hydrobromic acid. This mixture was stirred to make it homogeneous. After allowing the solution to stand for 3 days, pale yellow prismatic crystals were grown from the solution.

Crystal data

$(C_{11}H_7N_2O)_2[CdBr_4].2H_2O$
M_r = 834.42
Triclinic
$P\overline{1}$
a = 9.776 (2) Å
b = 10.740 (2) Å
c = 15.135 (3) Å
α = 71.69 (2)°
β = 87.93 (2)°
γ = 63.48 (2)°
V = 1339.7 (6) Å^3
Z = 2
D_x = 2.068 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5–22°
μ = 6.76 mm^{-1}
T = 293 K
Prismatic
0.16 × 0.14 × 0.13 mm
Pale yellow

Data collection

Siemens *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans, 6 reflections, $\Delta\psi = 10°$)
$T_{\min} = 0.519$, $T_{\max} = 0.900$
3749 measured reflections
3502 independent reflections
2673 observed reflections [$I \geq 3\sigma(I)$]
$R_{\text{int}} = 0.0209$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$
2 standard reflections monitored every 98 reflections intensity decay: $\leq 1\%$

Refinement

Refinement on *F*
$R = 0.034$
$wR = 0.039$
$S = 0.913$
2673 reflections
388 parameters
$w = 1/[\sigma^2(F) + 0.00903F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cd	0.24084 (4)	0.51148 (4)	0.24619 (4)	0.0382 (3)
Br1	−0.0112 (1)	0.7363 (1)	0.25035 (4)	0.0526 (5)
Br2	0.4138 (1)	0.4470 (1)	0.39653 (5)	0.0556 (5)
Br3	0.3500 (1)	0.5756 (1)	0.08989 (5)	0.0513 (5)
Br4	0.2241 (1)	0.2726 (1)	0.25779 (4)	0.0575 (6)
O1	0.8406 (4)	−0.4801 (4)	0.1028 (3)	0.063 (6)
N1	0.5184 (5)	−0.0321 (5)	0.1539 (3)	0.042 (4)
N2	0.7266 (5)	0.0273 (5)	0.0055 (4)	0.042 (3)
C1	0.4398 (6)	−0.0818 (6)	0.2208 (4)	0.055 (5)
C2	0.4697 (6)	−0.2268 (6)	0.2524 (4)	0.055 (5)
C3	0.5790 (6)	−0.3271 (6)	0.2159 (4)	0.046 (4)
C4	0.6589 (6)	−0.2756 (6)	0.1488 (4)	0.044 (4)
C5	0.7820 (6)	−0.3509 (6)	0.0958 (4)	0.044 (4)
C6	0.8190 (6)	−0.2329 (6)	0.0340 (4)	0.042 (4)
C7	0.9263 (6)	−0.2370 (6)	−0.0277 (4)	0.058 (5)
C8	0.9323 (6)	−0.1037 (6)	−0.0724 (4)	0.067 (5)
C9	0.8325 (6)	0.0210 (6)	−0.0550 (4)	0.054 (4)
C10	0.7215 (6)	−0.0994 (6)	0.0474 (4)	0.039 (4)
C11	0.6270 (6)	−0.1278 (6)	0.1188 (4)	0.041 (4)
O1′	0.6197 (4)	−0.1114 (4)	0.4108 (3)	0.073 (4)
N1′	1.1369 (5)	−0.2266 (5)	0.4868 (4)	0.037 (3)
N2′	0.9810 (5)	0.0820 (5)	0.3349 (4)	0.037 (3)
C1′	1.1863 (6)	−0.3625 (5)	0.5518 (4)	0.043 (3)
C2′	1.0893 (6)	−0.4232 (5)	0.5801 (4)	0.038 (3)
C3′	0.9336 (6)	−0.3450 (6)	0.5372 (4)	0.044 (4)
C4′	0.8878 (6)	−0.2073 (5)	0.4708 (4)	0.036 (4)
C5′	0.7368 (6)	−0.0976 (6)	0.4107 (4)	0.045 (4)
C6′	0.7651 (6)	0.0254 (6)	0.3509 (4)	0.037 (4)
C7′	0.6723 (6)	0.1571 (6)	0.2819 (4)	0.049 (4)
C8′	0.7376 (6)	0.2463 (6)	0.2383 (4)	0.047 (4)
C9′	0.8868 (6)	0.2063 (6)	0.2679 (4)	0.053 (5)
C10′	0.9171 (6)	−0.0046 (6)	0.3726 (4)	0.034 (3)
C11′	0.9935 (6)	−0.1545 (5)	0.4473 (3)	0.032 (4)
O1*w*	0.4754 (4)	0.2459 (4)	0.0593 (3)	0.057 (3)
O2*w*	0.3088 (4)	−0.0814 (4)	0.4423 (3)	0.066 (4)

Table 2. *Selected geometric parameters* (Å, °)

Cd—Br1	2.584 (1)	Cd—Br2	2.599 (1)
Cd—Br3	2.581 (1)	Cd—Br4	2.594 (1)
O1—C5	1.211 (7)	O1′—C5′	1.218 (8)
N1—C1	1.367 (8)	N1′—C1′	1.355 (6)
N1—C11	1.340 (8)	N1′—C11′	1.313 (7)
N2—C9	1.349 (8)	N2′—C9′	1.334 (6)
N2—C10	1.331 (8)	N2′—C10′	1.319 (9)
C4—C5	1.488 (8)	C4′—C5′	1.505 (6)
C5—C6	1.500 (9)	C5′—C6′	1.482 (9)
C10—C11	1.445 (9)	C10′—C11′	1.508 (6)
Br1—Cd—Br2	103.7 (1)	Br1—Cd—Br3	110.1 (1)
Br1—Cd—Br4	117.2 (1)	Br2—Cd—Br3	115.8 (1)
Br2—Cd—Br4	106.0 (1)	Br3—Cd—Br4	104.4 (1)
C1—N1—C11	119.0 (5)	C1′—N1′—C11′	119.0 (6)
C9—N2—C10	115.1 (5)	C9′—N2′—C10′	113.3 (6)
N1—C1—C2	121.5 (6)	N1′—C1′—C2′	121.6 (5)
N2—C9—C8	124.6 (6)	N2′—C9′—C8′	125.8 (6)
N2—C10—C6	124.4 (6)	N2′—C10′—C6′	126.5 (5)
N2—C10—C11	127.4 (6)	N2′—C10′—C11′	126.6 (6)
N1—C11—C10	128.3 (6)	N1′—C11′—C10′	127.3 (6)
N1—C11—C4	120.8 (6)	N1′—C11′—C4′	123.4 (5)
H1*w*1—O1*w*—H2*w*1	135 (3)	H1*w*2—O2*w*—H2*w*2	114 (3)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1*w*	0.85 (5)	1.88 (4)	2.716 (7)	169 (4)
O1*w*—H2*w*1···Br3	0.93 (4)	2.46 (4)	3.372 (5)	167 (3)
O2*w*—H1*w*2···O1′	0.86 (3)	2.29 (3)	2.948 (6)	134 (3)
O1*w*—H1*w*1···N2	1.16 (3)	1.79 (3)	2.848 (6)	149 (3)
O2*w*—H2*w*2···Br4	1.10 (3)	2.63 (4)	3.691 (4)	161 (3)
N1′—H1′N···O2*w*$^{\text{i}}$	0.88 (4)	1.83 (4)	2.703 (8)	171 (3)
O2*w*—H2*w*2···N2′$^{\text{ii}}$	1.10 (3)	2.59 (4)	3.090 (6)	107 (2)

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

The structure was refined using full-matrix least-squares techniques; H atoms were located from difference Fourier maps, positioned geometrically and included as riding atoms with fixed isotropic displacement parameters in the structure-factor calculations.

Data collection: Siemens diffractometer software (*P*3 4.21/V). Cell refinement: Siemens diffractometer software (*P*3 4.21/V). Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1188). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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