Mononuclear and dinuclear bromide–nitrite cadmium(II) complexes with related 1,4-diazabicyclo[2.2.2]octane ligands

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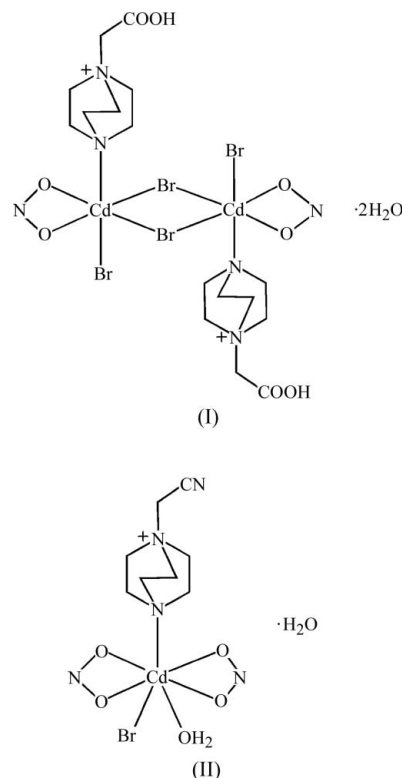The title compounds, di-μ-bromido-bis[bromido(1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane-κN^4)(nitrito-$\kappa^2 O,O'$)-cadmium(II)] dihydrate, $[Cd_2Br_4(C_8H_{15}N_2O_2)_2(NO_2)_2]\cdot 2H_2O$, (I), and aquabromido(1-cyanomethyl-4-aza-1-azoniabicyclo-[2.2.2]octane-κN^4)bis(nitrito-$\kappa^2 O,O'$)cadmium(II) monohydrate, $[CdBr(C_8H_{14}N_3)(NO_2)_2(H_2O)]\cdot H_2O$, (II), are two-dimensional hydrogen-bonded metal–organic hybrid complexes. In (I), the complex is situated on a centre of inversion so that each symmetry-related Cd^{II} atom is coordinated by two bridging Br atoms, one monodentate Br atom, one chelating nitrite ligand and one organic ligand, yielding a significantly distorted octahedral geometry. The combination of O—H$\cdots$O and O—H$\cdots$Br hydrogen bonds produces centrosymmetric $R_6^6(16)$ ring motifs, resulting in two-dimensional layers parallel to the ab plane. In contrast, the complex molecule in (II) is mononuclear, with the Cd^{II} atom seven-coordinated by two bidentate nitrite groups, one N atom from the organic ligand, one monodentate Br atom and a water O atom in a distorted pentagonal–bipyramidal environment. The combination of O—H$\cdots$O and O—H$\cdots$Br hydrogen bonds produces $R_5^4(14)$ and $R_3^3(8)$ rings which lead to two-dimensional layers parallel to the ac plane.

Comment

Certain metal–organic hybrid materials are of interest for their electric properties, such as ferroelectric, piezoelectric and dielectric (Planta & Unruh, 1993; Fu *et al.*, 2008; Ye *et al.*, 2009; Zhang *et al.*, 2010). A large variety of multifunctional ligands, such as 1,2,4-triazine, carboxylates and bipyridyl, have been used in order to prepare new metal–organic hybrid materials. Extended structures of cadmium(II) nitrate–organic ligand materials have been reported (Marlin *et al.*, 2006; Sharma & Clearfield, 2000; Lu *et al.*, 2005), but cadmium(II) nitrite–organic ligand materials are very rare. Additionally, previous studies have reported that 1,4-diazabicyclo[2.2.2]-

octane (DABCO) derivatives can go through phase transitions (Zhang *et al.*, 2009; Ye *et al.*, 2010). As part of an exploration of new metal–organic hybrid materials, a new DABCO derivative has been produced, namely 1-cyanomethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide. Novel cadmium(II) complexes were then synthesized using this ligand and the related 1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane ligand, together with nitrite and bromide.

Cadmium(II) complexes have rich coordination numbers and geometries because of the d^{10} configuration of the Cd^{II} ions. The structural diversity observed includes monomers (Choudhury *et al.*, 2003), dimers (Fuhr & Fenske, 1999) and coordination polymers (Thorn *et al.*, 2005). The title compounds are a cadmium(II) dimer with bromide bridges, di-μ-bromido-bis[bromido(1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane-κN^4)(nitrito-$\kappa^2 O,O'$)cadmium(II)] dihydrate, (I), and a cadmium(II) monomer, aquabromido-(1-cyanomethyl-4-aza-1-azoniabicyclo[2.2.2]octane-κN^4)bis-(nitrito-$\kappa^2 O,O'$)cadmium(II) monohydrate, (II), both of which
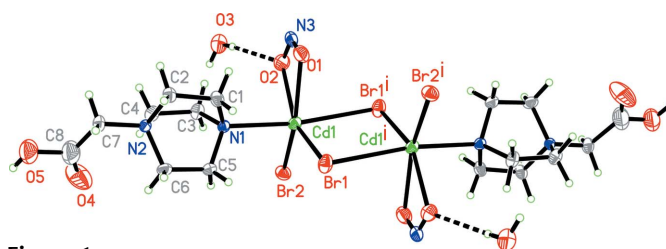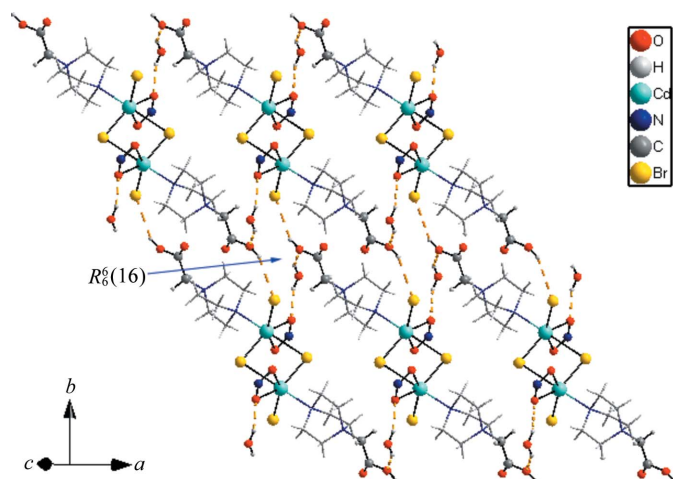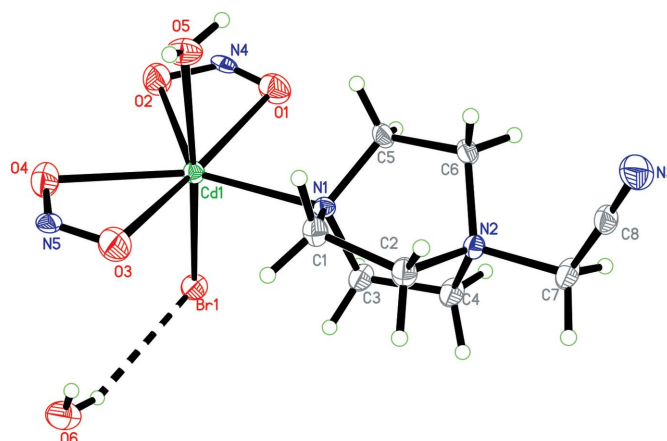

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level and dashed lines indicate O—H$\cdots$O hydrogen bonds. [Symmetry code: (i) $-x$, $-y + 1$, $-z + 1$.]

metal-organic compounds

Figure 2
A packing diagram for (I), showing the formation of $R_6^6(16)$ rings. Dashed lines represent O—H···O and O—H···Br interactions. The DABCO fragments are shown as sticks for clarity.
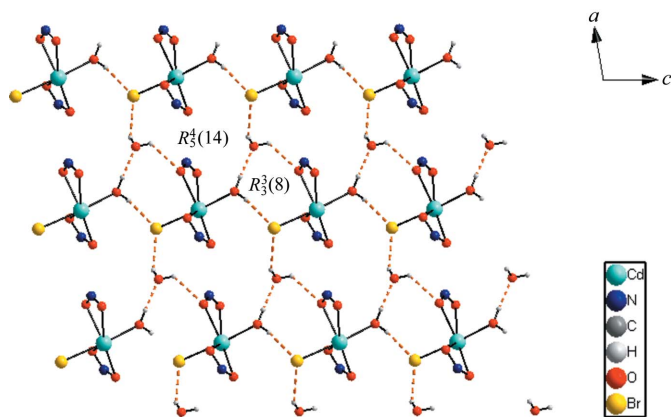

Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates an O—H···Br hydrogen bond.

are the first structurally examined cadmium complexes with these organic ligands.

Compound (I) consists of discrete neutral [Cd$_2$(1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane)$_2(\mu_2$-Br)$_2$Br$_2$(NO$_2$)$_2$] molecules and interstitial water molecules (Fig. 1). The dinuclear complex is distributed across a centre of inversion so that the asymmetric unit consists of one Cd^{II} cation, two bromide anions, one nitrite anion, one organic ligand and one lattice water molecule. Each Cd^{II} ion is sixfold coordinated by two O atoms from a bidentate nitrite ion, one N atom from the organic ligand and three bromide ions, which can be regarded as a somewhat distorted octahedral coordination geometry. One of the three bromide ligands is monodentate, while the other two are bridging, thus producing a tetranuclear Cd$_2$Br$_2$ dimeric unit. The two terminal bromide ligands are *trans* oriented with respect to the four-membered central bridge ring, and the two bridging bromide ligands and two Cd^{II} ions form a rectangular plane whose centre is located on a crystallographic centre of inversion. The Cd$_2$Br$_2$ rings in reported cadmium(II) dimers (Pickardt & Staub, 1999) are almost square because the Cd^{II} atom only has one kind of ligand other than Br, while in (I) the Cd$_2$Br$_2$ ring is rectangular since there are two quite different ligands besides Br, resulting in asymmetry of the Cd—Br bonds (Table 1). A similar Cd$_2$Br$_2$ unit with a terminal Br on each Cd has been observed previously in the compound di-μ-bromo-bis[bromo(di-2-pyridylmethanediol)cadmium(II)] trihydrate (Zhu *et al.*, 2000). The Cd—O bond distances within the nitrite ligand are slightly shorter than the Cd—N distance, which is the opposite of what is observed in the related complex [Cd(pyterpy)-(H$_2$O)(NO$_3$)$_2$] [pyterpy is 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine; Granifo *et al.*, 2004]. The two Br ligands and bidentate nitrite at the equatorial positions are almost coplanar, with a dihedral angle between the Cd1/Br1/Br2 and Cd1/O1/O2 planes of 7.3 (3)°. The axial N1—Cd1—Br1^i angle [symmetry code: (i) $-x, -y + 1, -z + 1$] deviates only modestly from 180°.

Molecules of (I) are linked into two-dimensional sheets parallel to the crystallographic *ab* plane through O—H···Br and O—H···O interactions which also form centrosymmetric $R_6^6(16)$ rings (Fig. 2). Carboxyl atom O5 of the organic ligand forms one donor hydrogen bond with a monodentate Br ligand from an adjacent dimer and also one acceptor hydrogen bond from a nearby lattice water molecule. The intermolecular O—H···Br hydrogen bonds (Table 2) serve to link the complexes into ladders, some of which run along [110] and others along [1$\bar{1}$0] depending on which layer one is in. Meanwhile, lattice water molecules act as hydrogen-bond donors to O2 atoms of the coordinated nitrite. The hydrogen bonds produced by the water molecules extend the ladders into two-dimensional hydrogen-bonded layers which then stack along [001], with no obvious interactions.

Although compound (II) has similar ligands, the structure of (II) is a Cd^{II} monomer with quite different coordination geometry. The Cd^{II} ion in (II) is seven-coordinate and the distorted pentagonal–bipyramidal coordination environment consists of one monodentate Br atom, one N atom of the organic ligand, four O atoms from two bidentate nitrite groups and one coordinated water molecule (Fig. 3). The asymmetric unit also includes one noncoordinated water molecule. The two coordinated nitrite groups at the equatorial positions are not coplanar, with a dihedral angle between the Cd1/O1/O2 and Cd1/O3/O4 planes of 12.3 (3)°, which is different from what is found in a related complex containing two nitrite ligands (Marandi *et al.*, 2005), although the ligands at the axial positions in the two complexes are different.

While the molecular structures of the Cd complexes in (I) and (II) are dissimilar, they do have similar intermolecular interactions. For both complexes, the uncoordinated water molecule is decisive for the crystal packing. In (II), intermolecular O—H···Br hydrogen bonds link discrete neutral molecules into chains along the *c* axis (Fig. 4). The free water atom (O6) acts as a hydrogen-bond donor, *via* atoms H6WA and H6WB, respectively, to atoms O2^{iii} and Br1, and also as a hydrogen-bond acceptor with O5^{iv} *via* atom H5WB^{iv}

Figure 4
A packing diagram for (II), showing the formation of $R_3^3(8)$ and $R_5^4(14)$ rings. Dashed lines represent O—H···O and O—H···Br interactions. The organic ligand fragments not involved in these interactions have been omitted for clarity.

[symmetry codes: (iii) $x + 1, y, z$; (iv) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$]. The combination of the O—H···O and O—H···Br hydrogen bonds generates alternating $R_5^4(14)$ and $R_3^3(8)$ rings, resulting in two-dimensional layers parallel to the *ac* plane.

Dielectric measurements of both compounds show no dielectric anomaly from 93 to 363 K, indicating no structural phase transitions in the measured temperature range.

Experimental

Bromoacetonitrile (0.1 mol, 12.00 g) was added to a CH_3CN solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.05 mol, 5.6 g) with stirring for 1 h at room temperature. 1-Cyanomethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide formed quickly as a white solid and was filtered off, washed with acetonitrile and dried (yield: 80%). Compounds (I) and (II) were prepared from aqueous solutions containing 1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide [for (I)] or 1-cyanomethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide [for (II)] (0.01 mol, 2.32 g), $CdSO_4$ (0.01 mol, 2.08 g), $Ba(NO_2)_2$ (0.01 mol, 2.29 g) and, additionally, imidazole (0.01 mol, 0.68 g) for (I). After removal of the precipitated $BaSO_4$, the resulting solution was allowed to evaporate for 18 [for (I)] or 6 d [for (II)] at room temperature, and colourless crystals suitable for X-ray analysis were obtained.

Compound (I)

Crystal data

$[Cd_2Br_4(C_8H_{15}N_2O_2)_2$- $(NO_2)_2]\cdot 2H_2O$		$\beta = 101.99\ (3)°$	
$M_r = 1014.91$		$V = 1505.9\ (5)\ Å^3$	
Monoclinic, $P2_1/n$		$Z = 2$	
$a = 8.7790\ (18)\ Å$		Mo $K\alpha$ radiation	
$b = 13.374\ (3)\ Å$		$\mu = 6.77\ mm^{-1}$	
$c = 13.113\ (3)\ Å$		$T = 293$ K	
		$0.2 \times 0.2 \times 0.2$ mm	

Data collection

Rigaku Mercury CCD diffractometer	15299 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) $T_{min} = 0.631$, $T_{max} = 1.000$	3461 independent reflections 2877 reflections with $I > 2\sigma(I)$ $R_{int} = 0.049$

Table 1
Selected geometric parameters (Å, °) for (I).

N1—Cd1	2.447 (5)	Br1—Cd1	2.6354 (9)
O1—Cd1	2.397 (6)	Br1—Cd1^i	3.0191 (10)
O2—Cd1	2.393 (6)	Br2—Cd1	2.5890 (10)
Cd1—Br1—Cd1^i	90.87 (3)	N1—Cd1—Br1	93.80 (12)
O2—Cd1—N1	90.73 (19)	N1—Cd1—Br1^i	172.29 (12)
O1—Cd1—N1	90.37 (19)	Br1—Cd1—Br1^i	89.13 (3)
N1—Cd1—Br2	93.99 (13)		

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5C···Br2^{ii}	0.85	2.75	3.569 (9)	162
O3—H3D···O2	0.85	2.13	2.932 (9)	158
O3—H3C···O5^{iii}	0.85	2.20	2.957 (12)	149

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	15 restraints
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 1.30$ e Å^{-3}
3461 reflections	$\Delta\rho_{min} = -1.10$ e Å^{-3}
172 parameters	

Compound (II)

Crystal data

$[CdBr(C_8H_{14}N_3)(NO_2)_2$- $(H_2O)]\cdot H_2O$		$\beta = 99.505\ (5)°$	
		$V = 1512.6\ (8)\ Å^3$	
$M_r = 472.58$		$Z = 4$	
Monoclinic, $P2_1/c$		Mo $K\alpha$ radiation	
$a = 7.343\ (2)\ Å$		$\mu = 4.12\ mm^{-1}$	
$b = 16.254\ (5)\ Å$		$T = 293$ K	
$c = 12.850\ (4)\ Å$		$0.2 \times 0.2 \times 0.2$ mm	

Data collection

Rigaku Mercury CCD diffractometer	16104 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) $T_{min} = 0.663$, $T_{max} = 1.000$	3458 independent reflections 3110 reflections with $I > 2\sigma(I)$ $R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	34 restraints
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{max} = 1.47$ e Å^{-3}
3458 reflections	$\Delta\rho_{min} = -0.86$ e Å^{-3}
190 parameters	

For (I), the carbon-bound H atoms were positioned with idealized geometry and treated as riding atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The water and carboxyl H atoms were found in difference Fourier maps; however, they were placed at idealized positions, with O—H = 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. Carboxyl atoms O4 and O5 showed significantly larger anisotropic displacement parameters than C8 that were elongated perpendicular to the carboxyl plane, suggesting possible disorder of the carboxyl group. Our attempt to model this disorder with two orientations did not

Table 3
Selected geometric parameters (Å, °) for (II).

N1—Cd1	2.413 (4)	O4—Cd1	2.424 (4)
O1—Cd1	2.443 (4)	O5—Cd1	2.401 (4)
O2—Cd1	2.376 (4)	Br1—Cd1	2.7187 (9)
O3—Cd1	2.403 (4)		
O5—Cd1—N1	86.75 (13)	O3—Cd1—O1	167.12 (16)
O3—Cd1—N1	89.43 (13)	N1—Cd1—O1	84.71 (14)
O3—Cd1—O4	51.57 (14)	O5—Cd1—Br1	175.22 (10)
O2—Cd1—O1	50.46 (15)	N1—Cd1—Br1	97.92 (9)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$WA\cdots$Br1[i]	0.85	2.50	3.352 (4)	175
O5—H5$WB\cdots$O6[ii]	0.85	2.02	2.731 (6)	140
O6—H6$WA\cdots$Br1	0.85	2.72	3.486 (5)	151
O6—H6$WB\cdots$O2[iii]	0.85	2.36	2.872 (6)	120

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x + 1, y, z$.

afford reasonable results. Considering that the carboxyl is a terminal group in the structure, this can be understood as dynamical disorder in a single potential well corresponding to the rotation of the carboxyl group around the C7—C8 bond. In the end, to maintain reasonable geometry and displacement parameters, similarity restraints with an s.u. value of 0.005 Å^2 were applied to the atomic displacement parameters of atoms O4, O5 and C8, and a rigid bond restraint with an s.u. value of 0.01 Å^2 was applied to the atomic displacement parameters of atoms O5 and C8.

For (II), positional parameters of all the carbon-bound H atoms were calculated geometrically and the atoms were allowed to ride with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). All the water H atoms were found in difference Fourier maps; however, they were placed at ideal positions, with O—H = 0.85 Å and U_{iso}(H) = 1.5U_{eq}(O). The O atoms in the nitrite groups showed large anisotropic displacement parameters that were elongated along the N—O bonds. The origin of this phenomenon is unknown, however, we do not believe it was caused by disorder because trying to model such disorder with two orientations did not afford an acceptable result. To maintain reasonable geometries as observed in similar known nitrite compounds, the N—O bonds were restrained to 1.25 (1) Å. Similarity restraints with an s.u. value of 0.01 Å^2 were applied to the atomic displacement parameters of the N and O atoms within each nitrite group. In addition, a rigid bond restraint with an s.u. value of 0.003 Å^2 was applied to the atomic displacement parameters of pairs of nitrite N and O atoms (s.u. = 0.002 Å for O2—N4).

For both compounds, data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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