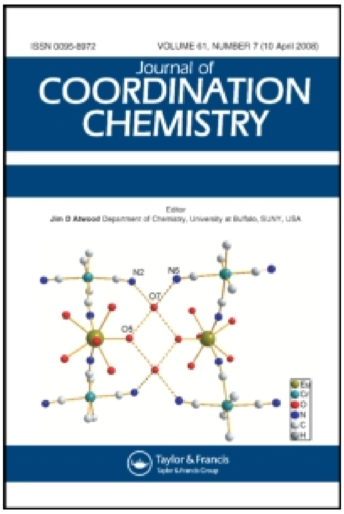

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X-ray study of two new cadmium acetato complexes

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Two new cadmium acetate compounds, $Cd(tpy)(Ac)_2 \cdot 2H_2O$ (**1**) and $Cd_2(bbip)_2(Ac)_3 \cdot 0.5S_2O_8 \cdot 2H_2O$ (**2**) (tpy = 2,2′,2″-terpyridine; bbip = 2,6-bis(benzimidazol-2-yl)pyridine; Ac = acetate), have been synthesized and their crystal structures determined. Compound **1** is monoclinic, $P2(1)/n$, $a = 8.4899(11)$, $b = 23.169(3)$, $c = 10.9224(14)$ Å, $\beta = 7.493(2)°$, $V = 2049.1(5)$ Å^3, $Z = 4$, $R = 0.037$ for 4552 N_i independent reflections and for 1619 N_o observed $[I > 2\sigma(I)]$ reflections. Compound **1** is monomeric, with a heptacoordinate cadmium ion bonded to two bidentate acetate groups and a tridentate tpy; two hydration water molecules complete the formula unit. Compound **2** is triclinic, $P\bar{1}$, $a = 10.8412(7)$, $b = 14.4051(9)$, $c = 15.5354(10)$ Å, $\alpha = 82.889(1)$, $\beta = 77.953(1)$, $\gamma = 85.805(1)°$, $V = 2351.73(3)$ Å^3, $Z = 2$, $R = 0.044$, $N_i = 9014$, $N_o = 6837$. The binuclear structure has two independent Cd atoms per asymmetric unit, two bbip tridentate ligands (one attached to each cation) and three acetate groups, displaying a range of different coordination features.

Keywords: Cadmium acetato complexes; Crystal structure

1. Introduction

Group 12 ions exhibit complete nd shells, with no stabilizing ligand-field effects to be expected in their stereochemistry. As a result, the geometries are determined solely by considerations of size and electrostatic or covalent binding forces, allowing coordination diversity of any accompanying ligand. In particular, carboxylate groups have proved to be highly versatile in this regard, and in the particular case of the acetate

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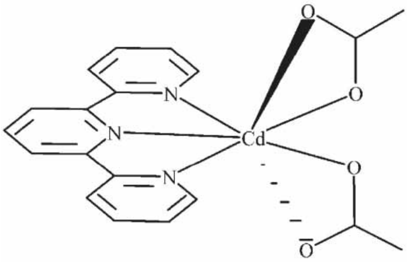
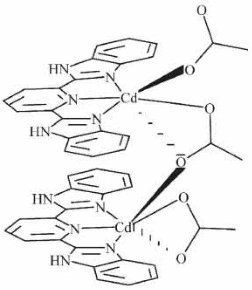


$+ 2H_2O$

(1)



$+ 2(H_2O) + 1/2\ (S_2O_8)$

(2)

anion a large number of compounds have been reported, in a variety of coordination modes.

Acetato complexes of Group 12 metal ions constitute a chapter in structural chemistry (256 structures reported in the November 2003 version of the Cambidge Structural Database (CSD), of which 187 correspond to Zn, 38 to Hg and 31 to Cd). The overwhelming predominance of zinc complexes reflects their biological interest due to the presence of the cation in many enzyme active sites, very often associated with the presence of a carboxylate group [1]. However, despite the lower interest, Cd and Hg complexes seem to be more interesting from a structural point of view because of the ability of these cations to modify both coordination numbers and geometries. As an example, we have recently reported a number of such coordination complexes obtained through the $Cd(CH_3COO)_2 + K_2S_2O_8 + L$ (L = organic base) system, containing either acetate or peroxodisulfate, or both [2,3].

Further exploration of the system resulted in the preparation of two new acetato complexes, $Cd(tpy)(Ac)_2 \cdot 2H_2O$ (**1**) and $Cd_2(bbip)_2(Ac)_3 \cdot 0.5S_2O_8 \cdot 2H_2O$ (**2**) (tpy = 2,2′,2″-terpyridine; bbip = 2,6-bis(benzimidazol-2-yl)pyridine; Ac = acetate), and their novel features are reported here.

2. Experimental

2.1. *Syntheses*

2.1.1. $Cd(tpy)(Ac)_2 \cdot 2H_2O$, 1. Reaction of an aqueous solution of $Cd(CH_3COO)_2 \cdot 2H_2O$ and $K_2(S_2O_8)$ with a solution of tpy in methanol (all reactants at a concentration of 0.050 M) resulted in a crystalline material that was not suitable for X-ray diffraction. Dissolution in hot dimethylformamide gave, after a few days, ill-formed crystals of different shapes. The best corresponded to a prismatic morphology and were separated from the rest under a microscope. All the crystals scrutinized from this subset belonged to the same phase (1), but the quality was in all cases poor and the specimen finally used for data collection provided only 35% of observed $[I > 2\sigma(I)]$ reflections.

2.1.2. $Cd_2(bbip)_2(Ac)_3 \cdot 0.5S_2O_8 \cdot 2H_2O$, 2. Diffusion of an aqueous solution of $Cd(CH_3COO)_2 \cdot 2H_2O$ and $K_2(S_2O_8)$ into a solution of bbip in dimethylformamide (all reactants at a concentration of 0.050 M) gave, on standing, two types of prismatic crystals; pale yellow ones corresponding to the already published $Cd(bbip)_2$ [4], and colorless ones corresponding to compound **2**.

The coexistence of different crystallographic forms in the final products made their chemical analysis (performed on selected subsets of similar morphology) very difficult and prevented further complementary studies in both compounds.

2.2. *Materials and measurements*

All starting materials were reagent quality and used without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA 1108 instrument.

2.3. *Elemental analysis*

The formulation of both compounds was supported by elemental analysis and, ultimately, by structure resolution by single-crystal X-ray analysis. Anal. Calcd. for **1**(%): C, 45.66; H, 4.24; N, 8.41. Found: C, 45.7; H, 4.3; N, 8.4. Anal. Calcd. for **2**(%): C, 45.69; H, 3.40; N, 12.11. Found: C, 45.5; H, 3.4; N, 12.0.

2.4. *Structure determination*

Unique room-temperature diffractometer data sets were collected for both structures using monochromatic Mo Kα radiation, $\lambda = 0.7107$ Å, $T = 295$ K, with a Bruker Smart Apex CCD diffractometer ($\omega/2\theta$ scan mode). Structure resolution was achieved by direct methods and Fourier difference syntheses. The structures were refined by least-squares procedures on F^2, with anisotropic displacement parameters for non-H atoms. Hydrogen atoms unambiguously defined by the stereochemistry were placed at their calculated positions and allowed to ride onto their host carbons in both coordinate and thermal parameters (C–H: 0.92, 0.96 Å; N–H: 0.86 Å). Those corresponding to the aqua molecules were located in a Fourier map and refined with similar restraints [O–H: 0.86(2) Å]. All calculations to solve and refine the structures were carried out using the programs SHELXS97 [5], SHELXL97 [6] and SHELXTL/PC [7]. Full use was also made of the Cambridge Crystallographic Data Centre (CCDC) package for searching in the CSD [8].

Crystal and structure refinement data are given in table 1, selected bond lengths in table 2 and hydrogen bonding data in table 3. Supplementary material has been deposited as CIF files at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, under codes CCDC 237019 and 237020.

3. Results and discussion

Compound **1** is monomeric and has a heptacoordinate cadmium center (figure 1) bonded to two chelating acetate groups and a tridentate tpy with two hydration water molecules completing the formula unit. Sevenfold coordination to cadmium is not uncommon but compound **1** exhibits a few special characteristics: it is the first

Table 1. Crystal data and structure refinement details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{19}H_{21}CdN_3O_6$	$C_{44}H_{39}Cd_2N_{10}O_{12}S$
Formula weight	499.79	1156.71
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/n$	P
A (Å)	8.4899(11)	10.8412(7)
B (Å)	23.169(3)	14.4051(9)
c (Å)	10.9224(14)	15.5354(10)
α°	90.0	82.8890(10)
β°	107.493(2)	77.9530(10)
γ°	90.0	85.8050(10)
V (Å^3)	2049.1(5)	2351.7(3)
Z	4	2
D_c (g cm^{-3})	1.620	1.634
μ (mm^{-1})	1.106	1.021
$F(000)$	1008	1162
Crystal size (mm^3)	0.24 × 0.16 × 0.10	0.30 × 0.20 × 0.16
θ range (°)	1.76 to 28.07	1.43 to 27.95
Index ranges	$-11 \le h \le 10$	$-13 \le h \le 14$
	$-28 \le k \le 29$	$-18 \le k \le 9$
	$-10 \le l \le 13$	$-19 \le l \le 18$
N_t, N_i [R_i], N_o	12 137, 4552 [0.0715], 1619	10 974, 9014 [0.0129], 6837
Absorption correction	Multiscan	Multiscan
Data/parameters	4552/277	9014/638
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	$S = 0.856$	$S = 0.967$
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0370$, $wR_2 = 0.0433$	$R_1 = 0.0439$, $wR_2 = 0.1203$
R indices (all data)	$R_1 = 0.1278$, $wR_2 = 0.0514$	$R_1 = 0.0569$, $wR_2 = 0.1278$
Max./min.$\Delta\rho$e Å^{-3})	0.553 and –0.426	0.911 and −0.632

N_t, total number of reflections measured; N_i, number of independent reflections; N_o, number of observed [$I > 2\sigma\ (I)$] reflections; R_i, internal consistency index.
$R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}$; $S = \{\sum [w(F_0^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

Table 2. Selected bond lengths (Å) for **1** and **2**.

1						
	Cd–N(1)	2.387(4)	Cd–O(2Δ)	2.314(3)	C(1A)–O(2A)	1.254(6)
	Cd–N(2)	2.355(3)	Cd–O(1B)	2.327(3)	C(1B)–O(1B)	1.251(5)
	Cd–N(3)	2.383(4)	Cd–O(2B)	2.432(3)	C(1B)–O(2B)	1.242(5)
	Cd–O(1A)	2.477(3)	C(1A)–O(1A)	1.247(5)		
2						
	Cd(1A)–N(1A)	2.366(3)	Cd(1B)–N(3B)	2.342(3)	S(1)–O(4)	1.603(6)
	Cd(1A)–N(2A)	2.327(3)	Cd(1B)–O(1Y)	2.341(3)	C(1X)–O(1X)	1.256(6)
	Cd(1A)–N(3A)	2.349(4)	Cd(1B)–O(2Y)	2.380(4)	C(1X)–O(2X)	1.237(6)
	Cd(1A)–O(1X)	2.469(3)	Cd(1B)–O(1Z)	2.183(3)	C(1Y)–O(1Y)	1.254(5)
	Cd(1A)–O(2X)	2.240(3)	S(1)–O(1)	1.388(5)	C(1Y)–O(2Y)	1.240(6)
	Cd(1A)–O(1Y)	2.227(3)	S(1)–O(2)	1.384(4)	C(1Z)–O(1Z)	1.263(5)
	Cd(1B)–N(1B)	2.348(3)	S(1)–O(3)	1.400(5)	C(1Z)–O(2Z)	1.228(6)
	Cd(1B)–N(2B)	2.345(3)	O(4)–O(4)$^{\#1}$	1.302(11)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+1, -y+2, -z$.

heptacoordinated cadmium complex having tpy as a ligand (the only two known Cd tpy complexes [9,10] are pentacoordinate), as well as the first one to display two purely chelating acetates. There are four reported cases with such a $Cd(Ac)_2$ binding mode where the cadmium center is either six- [11,12] or eight-coordinate [13,14].

Table 3. Hydrogen bonds [Å and °] in **1** and **2**.

D–H · A	*d*(D–H)	*d*(H · A)	*d*(D · A)	(< DHA)
1				
O(1W)–H(1WA) · · · O(2W)	0.88(2)	1.98(2)	2.828(5)	161(4)
O(1W)–H(1WB) · · · O(2A)$^{\#1}$	0.88(2)	1.97(2)	2.816(5)	160(5)
O(2W)–H(2WA) · · · O(1B)$^{\#2}$	0.87(2)	1.97(2)	2.836(5)	175(6)
O(2W)–H(2WB) · · · O(1A)$^{\#3}$	0.85(2)	2.15(3)	2.919(5)	150(5)
2				
N(4A)–H(4AB) · · · O(1X)$^{\#4}$	0.86	1.98	2.797(5)	159
N(4B)–H(4BB) · · · O(2)$^{\#5}$	0.86	1.94	2.738(5)	153
N(5B)–H(5BB) · · · O(2Z)$^{\#6}$	0.86	1.90	2.755(5)	174
N(5A)–H(5AB) · · · O(1W)$^{\#7}$	0.86	1.92	2.776(7)	174
O(1W)–H(1WA) · · · O(2W)$^{\#8}$	0.86(1)	1.86(3)	2.680(7)	160(8)
O(1W)–H(1WB) · · · O(1)$^{\#9}$	0.85(1)	2.19(3)	3.020(8)	165(8)
O(2W)–H(2WA) · · · O(3)	0.85(1)	2.10(2)	2.944(8)	175(5)
O(2W)–H(2WB) · · · O(2Z)$^{\#10}$	0.85(1)	1.94(3)	2.750(6)	160(6)

Symmetry transformations used to generate equivalent atoms: $^{\#1}x-1, y, z$; $^{\#2}x, y, z+1$; $^{\#3}x-1/2, -y+1/2, z+1/2$; $^{\#4}-x+2, -y, -z+1$; $^{\#5}x+1, y-1, z$; $^{\#6}-x+2, -y+1, -z$; $^{\#7}-x+1, -y+1, -z+1$; $^{\#8}x, y, z+1$; $^{\#9}-x+1, -y+2, -z+1$; $^{\#10}x-1, y, z$.

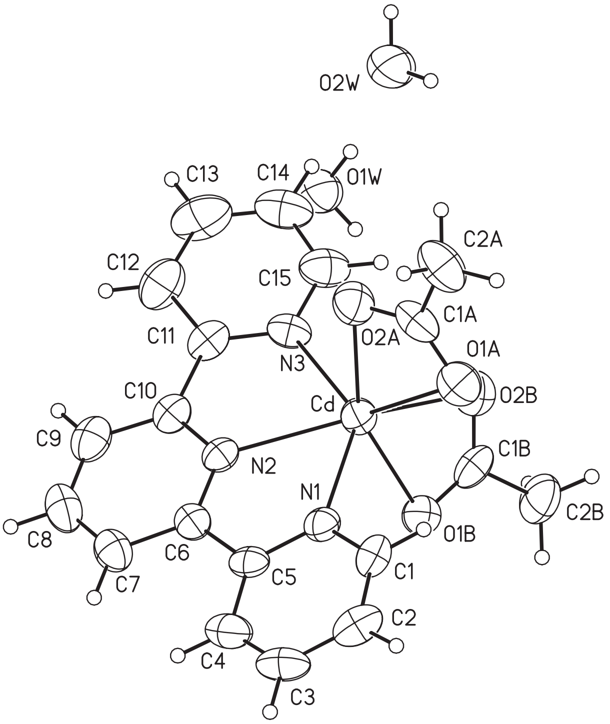


Figure 1. Molecular drawing of **1** showing the numbering scheme used to describe the monomers. Thermal ellipsoids shown at a 50% level.

Distances to the cation are within the expected values (table 2), with both acetates presenting a similar asymmetric mode of coordination: one short and one long bond distance (Cd–O_{acet}: 2.314(3), 2.477(3) Å and 2.327(3), 2.432(3) Å, for units A and B, respectively).

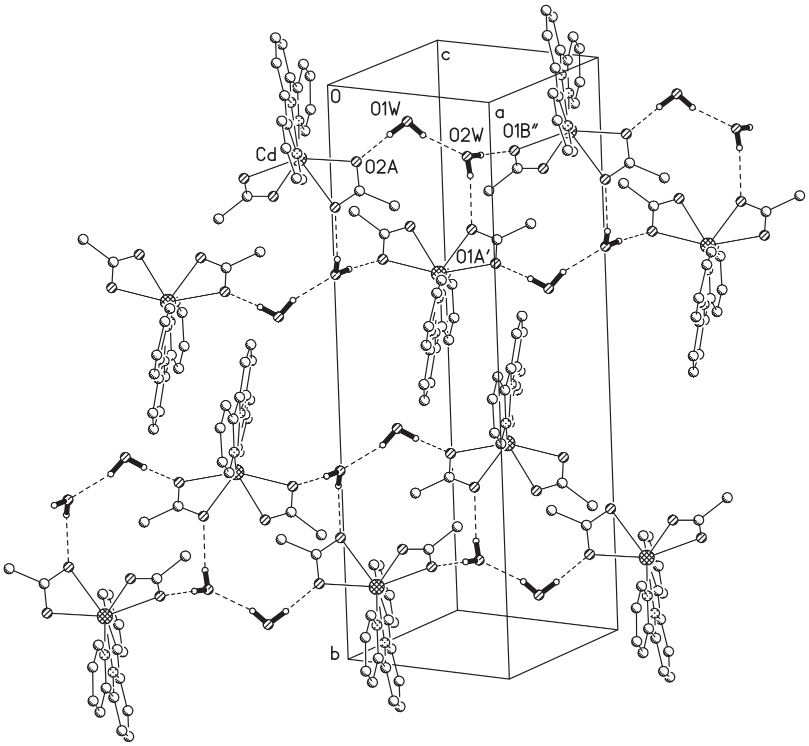


Figure 2. Packing view of **1** (direction of strips: [−101]). Note in the cell center the aromatic π–π contacts linking strips along ***b***. Hydrogen atoms not involved in H-bonding not drawn, for clarity.

The tpy ligand is not planar; due to coordination strain the molecule is bent into a concave shape, the central pyridyl group subtending dihedral angles of 4.7(1) and 16.7(1)° to the lateral ones.

The rigid character of the tpy bite leads Cd–N bond lengths in **1** to follow the general trend of Cdtpy complexes; that is, to have their $\text{Cd–N}_{\text{central}}$ bond slightly shorter than the $\text{Cd–N}_{\text{lateral}}$ (2.357 *vs* 2.390 and 2.385 Å in **1**, in consonance with 2.325 *vs* 2.353 and 2.368 Å and 2.405 *vs* 2.475 and 2.493 Å in complexes reported previously [9,10]. The symmetry displayed in the $\text{Cd–N}_{\text{lateral}}$ bond lengths is characteristic of tpy compounds coordinated to transition metals. (A search in the November 2003 version of the CSD gave 253 well-characterized complexes of this sort (R less than 0.05), where less than 6% have lateral asymmetry in coordination.)

The two hydration water molecules have an active role in H-bonding, connecting monomers together along the crystallographic [−101] direction, to form broad H-bonded double chains or strips (figure 2). These chains interact with each other along the crystallographic b direction through a π–π contact arising from partial overlap of neighboring centrosymmetrically related terpyridine units, which maintain a nearly "graphitic" distance (*ca* 3.40 Å) to each other. The interaction is of the "slipped" or "parallel displaced" type [15], with a slippage angle (subtended by the vector joining the displaced ring centers and one of the ring normals) of *ca* 23° (figure 3).

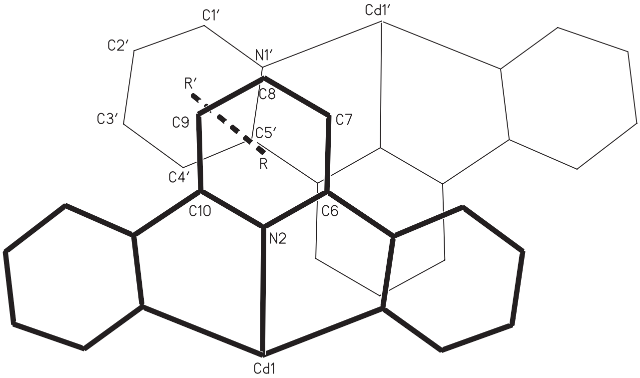


Figure 3. Close-up view of the aromatic π–π contacts in **1** showing ligand overlap. R and R′ are the ring centers. Symmetry code: ′2 – *x*, –*y*, –*z*.

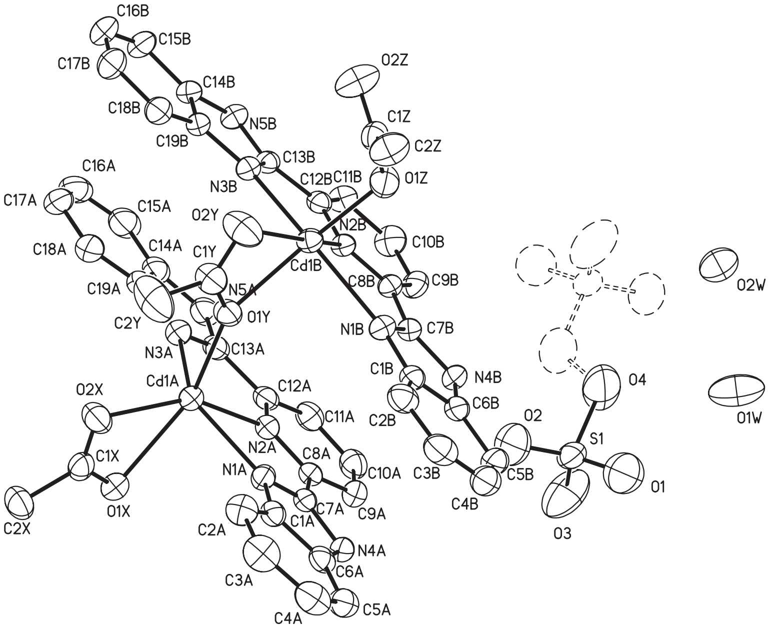


Figure 4. Displacement ellipsoid plot of **2** (at 50% level) showing the way in which the dinuclear entities build up. The symmetry-generated part of the pds counterion is shown in broken lines.

Compound **2** (figure 4) is binuclear with two independent Cd atoms, Cd(1A) and Cd(1B), per asymmetric unit, two bbip tridentate ligands (one unit attached to each cation) and three acetate groups displaying a range of coordination. One is monodentate to Cd(1B), another bidentate to Cd(1A), and the third bidentate to Cd(1B) while binding to Cd(1A) through one shared oxygen, thus acting as a bridge between both metals. (This chelato-bridging mode has already been reported in four other cadmium acetates [16–19].) The result of this coordination scheme is a pair of cationic centers surrounded by six neighbors each, in a highly distorted geometry hard to describe as deformation of a regular polyhedra. They share, however, a common characteristic:

the three nitrogens from bbip and the three oxygens from the acetato groups define sets of planes roughly perpendicular to each other [angle between l.s. planes: 84.2(3)° (unit A); 86.7(3)° (unit B)]. The monodentate acetate on Cd(1A) follows the traditional pattern of correlating a short Cd–O coordination distance with a long C–O one. The purely bidentate acetate bound to Cd(1B) shows the typical asymmetry in coordination to the cation described in **1** but associated to a direct (rather than the usual inverse) asymmetry in the carboxylate C–O groups. No clear reasons for this unusual behavior could be found. Finally, there is the chelato-bridging acetate that presents only slight differences in its chelato side [Cd–O: 2.342 and 2.381 Å to Cd(1A)] and a notably shorter distance in its bridge to Cd(1B) (Cd–O: 2.226 Å).

The bbip molecules bind *cis* to the metal atoms in such a way as to have their planes almost parallel to each other (angle between best planes *ca* 1.8°) and rotated 29.1° along the line connecting both metallic centers. Both the large overlap of the aromatic rings and the graphitic distance between mean planes (*ca* 3.4 Å) suggest strong intramolecular π–π interaction between the ligands.

This *cis* positioning of two planar ligands bound to transition metals in a binuclear molecule is not common. We could find only four such cases in the literature (none with Cd): two Mn complexes, one with tpy [20] and another with quinquerpyridine [21]; a Ru complex with tpy [22] and finally an Fe complex with quaterpyridine [23].

The two bbip ligands coordinate in a slightly different way, Cd–N_{bbip} distances being even around Cd(1B), in agreement with the results found by Harvey *et al.* [24], but showing slight differences around Cd(1A).

The binuclear, singly-charged cationic group is balanced by half of a peroxodisulfate (pds) ion, located on a center of symmetry, and thus accounting for one electron per asymmetric unit. This counterion role of pds in metallorganic compounds, though not novel, is not frequent; only very recently have some metallorganic compounds of this sort been described [25].

The geometry of the anion in **2** shares the special characteristics shown in previously reported structures [2,3,25], namely:

1. The ion presents an "almost" planar S–O–O–S core (in this case, because of symmetry centering, "exactly" so) as measured by the dihedral angle S1–O4–O4′–S4′ (180°).
2. One of the external oxygens O_{ext} [in this case O(1)] is distinguished by the fact that its O_{ext}–S–O_{core} angle is some 10° smaller than the remaining two: O1–S1–O4 [95.2(4)°] *vs* O2–S1–O4 [108.1(4)°] and O3–S1–O4 [108.0(5)°].
3. The angle lies almost in the core plane (torsion angle *ca* 180°): O1–S1–O4–O4′ [–166.5(13)°] *vs* O2–S1–O4–O4′ [–44.7(15)°] and O3–S1–O4–O4′ [77.0(13)°].

Another conspicuous feature in the pds anion is the prolate displacement factor displayed by the internal oxygen O4, normal to the molecular planar core (S1–O4–O4′–S1′), probably suggesting "out-of-plane" disorder, not large enough to be described by a split model.

Given the large number of potential donors and acceptors, the hydrogen bonding scheme is rather complex (table 3). There are two types of interactions present, according to their effects: the first involves N(4A) and N(5B) as donors and O(1X)[2 – *x*, –*y*, 1 – *z*] and O(2Z)[2 – *x*, 1 – *y*, –*z*] as acceptors. These interactions link the dimers tightly together to form chains along [01–1] (figure 5). This family of 1D structures is in turn

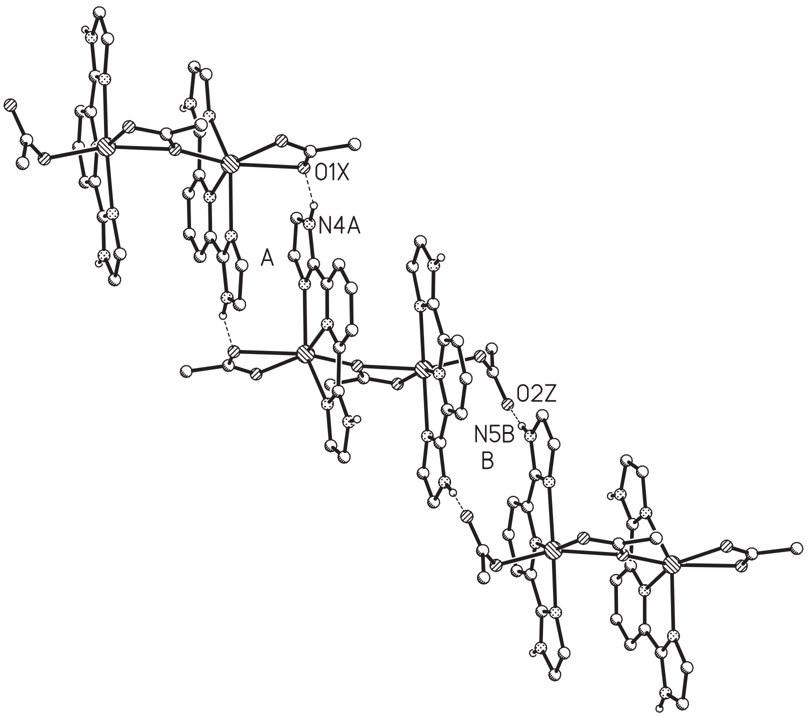


Figure 5. Packing view of **2** showing molecules tightly linked into strips running along [−101]. Terminal benzyl groups in bbip and nonrelevant hydrogen atoms are not shown, for clarity.

connected by a very complex network of H-bonds involving the water molecules and the pds ion, ending up in a tightly linked 3D structure. π–π contacts linking aromatic wings of neighboring symmetry-related binuclear entities with one another, bbip(A)–bbip(A[$2 - x, -y, 1 - z$]) and bbip(B)–bbip(B[$2 - x, 1 - y, -z$]), also contribute (figure 6b,c). As well as the intramolecular Π–Π interaction already described, these intermolecular interactions are also of the "slipped" or "parallel displaced" type [15], this time with a slippage angle of 23.5°.

4. Conclusions

We have described the first heptacoordinate Cdtpy compound, which, at the same time, is the first cadmium monomer to display two chelating acetates in its coordination polyhedron. A very unusual *cis* conformation of bbip (in fact of *any* related planar organic ligand) leading to a clear intramolecular π–π interaction has been found in the second binuclear compound reported. In both structures a prolific H-bonding system, as well as a variety of aryl–aryl contacts, provides for packing stabilization. These results confirm that Group 12 cations complexed to carboxylate groups and polydentate aromatic ligands are good candidates for disclosing novel features in their coordination as well as in their three-dimensional self-assembly.

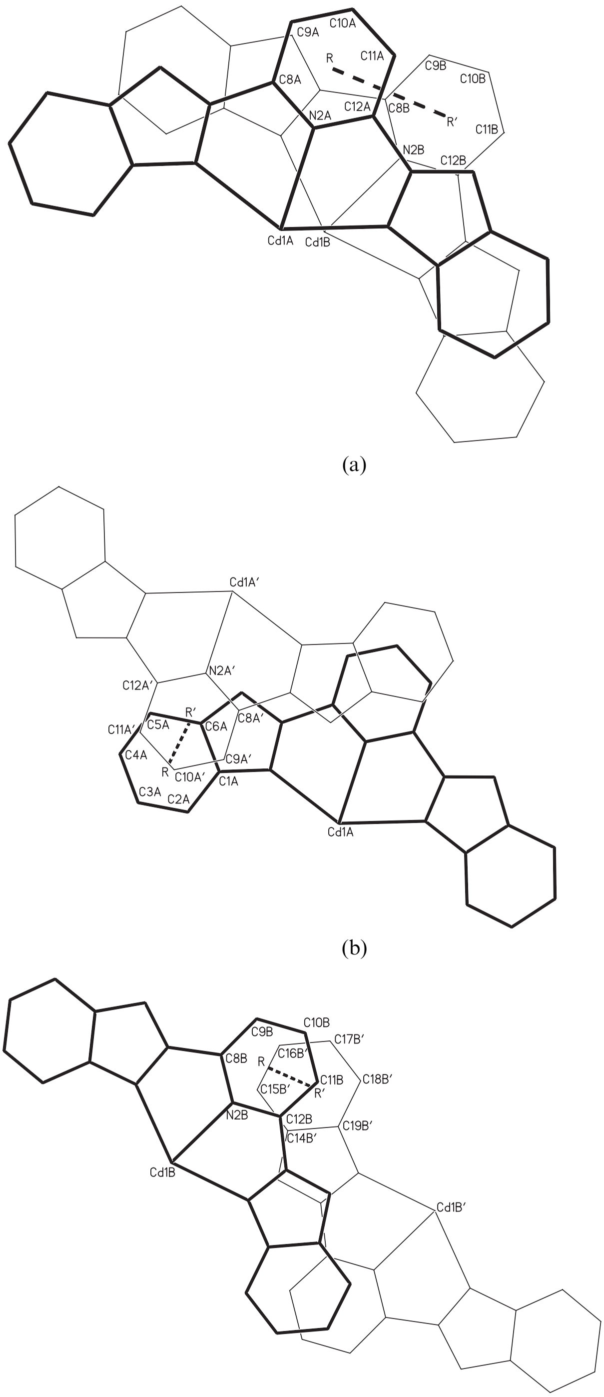


Figure 6. Close-up view of the aromatic π–π contacts in **2**, showing ligand overlap. R and R′ are the ring centers. (a) Intramolecular contact between bbips (A) and (B). (b) Intermolecular contact between bbips (A) and (A′). Symmetry code: ′$2 - x$, $-y$, $1 - z$. (c) Intermolecular contact between bbips (B) and (B′). Symmetry code: ′$2 - x$, $1 - y$, $-z$.

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