

## Di- $\mu$ -acesulfamato- $\kappa^3N,O:O;\kappa^3O:-N,O$ -bis[(acesulfamato- $\kappa^2N,O$ )bis(3-methylpyridine)cadmium(II)]

Zarife Sibel Şahin,<sup>a\*</sup> Hasan İçbudak<sup>b</sup> and Şamil Işık<sup>a</sup>

<sup>a</sup>Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, TR-55139 Samsun, Turkey, and <sup>b</sup>Department of Chemistry, Arts and Sciences Faculty, Ondokuz Mayıs University, TR-55139 Samsun, Turkey  
Correspondence e-mail: sgul@omu.edu.tr

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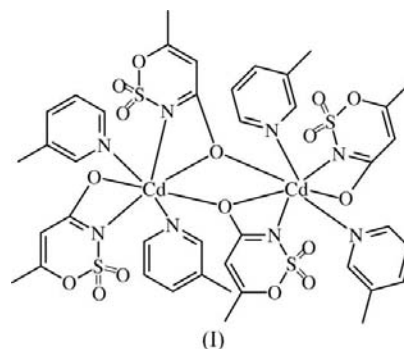
In the structure of the title compound,  $[\text{Cd}_2(\text{C}_4\text{H}_4\text{NO}_4\text{S})_2(\text{C}_6\text{H}_7\text{N})_2]$ , the dinuclear  $\text{Cd}^{\text{II}}$  complex is located on a twofold axis with two  $\text{Cd}^{2+}$  ions bridged by two oxide O atoms. Each  $\text{Cd}^{2+}$  ion is additionally coordinated in an equatorial plane by two N and three O atoms of the acesulfamate ligands and axially by two N atoms of the 3-methylpyridine ligands, resulting in a distorted pentagonal bipyramidal coordination. We present here an example of a supramolecular assembly based on hydrogen bonds in a mixed-ligand metal complex; intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds give rise to  $R_4^4(40)$  rings, which lead to one-dimensional chains.

### Comment

Acesulfame is an oxathiazinone dioxide and is systematically named as 6-methyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide; it is also known as 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-one 2,2-dioxide or acetosulfam. It was discovered by chemist Karl Clauss in 1967 (Clauss & Jensen, 1973) and has been widely used as a noncaloric artificial sweetener since 1988, after the FDA (US Food and Drug Administration) granted approval (Duffy & Anderson, 1998). Many countries have approved the use of acesulfame K, *viz.* the potassium salt of acesulfame, in soft drinks, candies, toothpastes, mouthwashes, cosmetics and pharmacological preparations (Mukherjee & Chakrabarti, 1997). The acesulfamate ion ( $\text{acs}^-$ ) has several potential donor atoms and thus, as a polyfunctional ligand, it can engage in N,  $\text{O}_{\text{CO}}$ ,  $\text{O}_{\text{OSO}}$  or O coordination with different metal ions. In order to examine the coordination behaviour of acesulfamate in metal complexes, the title complex, (I), has been synthesized and its crystal structure is presented here.

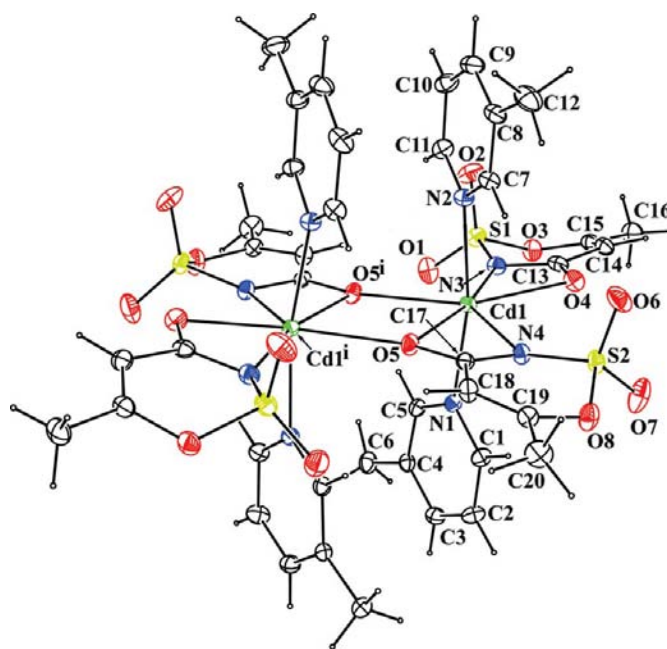
The ongoing research carried out in our laboratory on the coordination behaviour of the acesulfamate ligand in transition metal complexes has revealed that four different bonding patterns may exist: *N*-coordination through imino N (İçbudak, Bulut *et al.*, 2005), *O*-coordination through oxide O (İçbudak

*et al.*, 2006), *N,O*-coordination through imino N and oxide O as a bidentate ligand (Bulut *et al.*, 2005), and the acesulfamate ion remaining outside the coordination sphere when the secondary ligand has strong chelating properties (İçbudak, Heren *et al.*, 2005). Compound (I) is the first complex containing the bridging acesulfamate ligand.

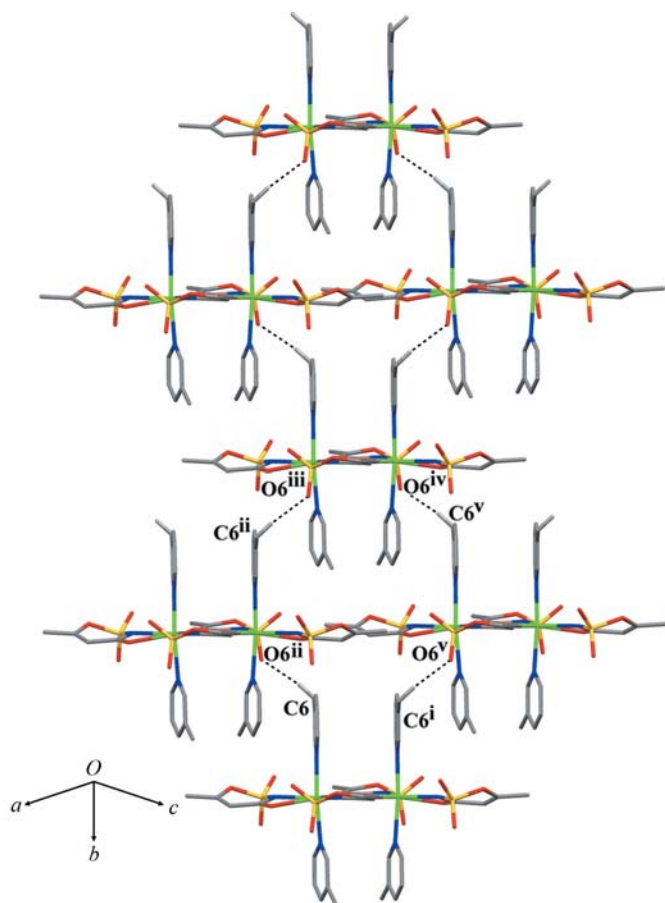


In complex (I), located across a twofold axis, one of the crystallographically independent acesulfamate ligands shows bidentate behaviour and coordinates to a  $\text{Cd}^{\text{II}}$  ion both through the imino N and the oxide O atom. The other acesulfamate ligand behaves as a bridging ligand between two  $\text{Cd}^{\text{II}}$  ions *via* the oxide O atom and also coordinates to one of the  $\text{Cd}^{\text{II}}$  ions *via* the imino N atom (see scheme and Fig. 1).

Both  $\text{Cd}^{2+}$  ions are coordinated by three O atoms and two N atoms of the acesulfamate ligands and two N atoms of the 3-methylpyridine ligands. Thus, four four-membered chelate rings ( $\text{Cd1/N3/C13/O4}$  and  $\text{Cd1/N4/C17/O5}$ , and their

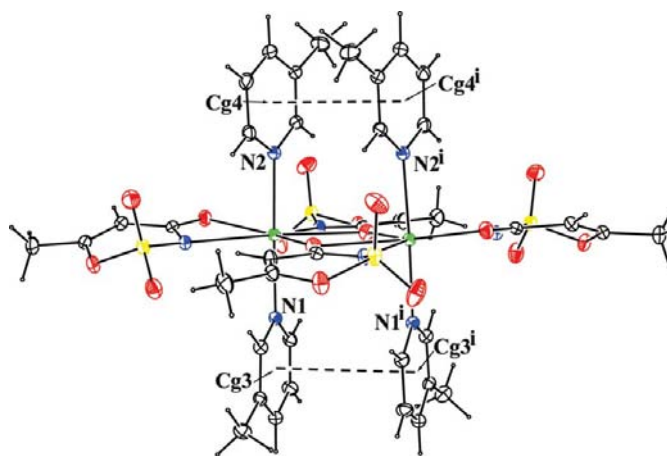


**Figure 1**  
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. (The symmetry code is as in Table 2.)


**Figure 2**

Part of the crystal structure of (I), showing the formation of a chain of edge-fused  $R_4^+(40)$  rings. Hydrogen bonds are indicated by dashed lines. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (i)  $1 - x, y, \frac{1}{2} - z$ ; (ii)  $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $x, -1 + y, z$ ; (iv)  $1 - x, -1 + y, \frac{1}{2} - z$ ; (v)  $-\frac{1}{2} + x, -\frac{1}{2} + y, z$ .]

symmetry-related counterparts) are formed. Two of the O atoms of the acesulfamate ligands act as a  $\mu_2$ -bridge connecting two  $\text{Cd}^{2+}$  ions, thus forming a rhomboidal  $\text{Cd}_2\text{O}_2$  ring. The  $\text{Cd} \cdots \text{Cd}^{\text{i}}$  [symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ ] distance is 4.0526 (5) Å, and the dihedral angles between the rhomboid ring and the four-membered chelate rings are 11.07 (4) and 2.31 (1)°, respectively. Each  $\text{Cd}^{2+}$  ion is seven-coordinate, forming a distorted pentagonal bipyramid, with atoms N3, O4, N4, O5 and O5<sup>i</sup> forming the distorted pentagonal plane. The coordination number seven for  $\text{Cd}^{\text{II}}$  is rare because of increased ligand–ligand repulsion, weaker bonds and, usually, reduced crystal field stabilization in comparison with octahedral complexes. Coordination number seven is most commonly found in discrete complexes of second- and third-row transition metals, such as lanthanides and actinides (Arndt *et al.*, 2002; Han *et al.*, 1999). The three known coordination geometries for seven-coordination are: (i) pentagonal bipyramidal (Rodesiler *et al.*, 1985), (ii) monocapped octahedral with a seventh ligand added to a rectangular face (Chen *et al.*, 2008) and (iii) monocapped trigonal prismatic with a seventh ligand added to a rectangular face (Yeşilel *et al.*, 2007). These geometries are considered to have approximately


**Figure 3**

Part of the crystal structure of (I), showing the  $\pi$ – $\pi$  interactions (dashed lines) between pyridine rings. (The symmetry code is as in Table 2.)

equal *a priori* probabilities (Park *et al.*, 1970). The first coordination geometry, *viz.* (i), is observed in (I). The pentagonal bipyramidal coordination of the  $d^3sp^3$ -hybridized  $\text{Cd}^{2+}$  ion is seldom observed: an octahedral  $d^2sp^3$  hybridization with six coordination bonds is usually preferred. The acesulfamate rings adopt a half-chair conformation, as evidenced from the puckering parameters (Cremer & Pople, 1975):  $Q = 0.391$  (3) Å,  $\theta = 62.5$  (4)° and  $\varphi = 12.2$  (6)° for S1/O3/C15/C14/C13/N3 and  $Q = 0.319$  (2) Å,  $\theta = 58.3$  (5)° and  $\varphi = 13.9$  (6)° for S2/O8/C19/C18/C17/N4.

Crystal packing is achieved *via* intermolecular hydrogen bonding (Fig. 2 and Table 2). The intramolecular C18–H18  $\cdots$  O1<sup>i</sup> hydrogen bond can be described as an  $S(8)$  ring in graph-set notation (Bernstein *et al.*, 1995). Atom C6 acts as a hydrogen-bond donor, *via* atom H6C, to atom O6 in the molecule at  $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ , thus forming  $C(9)$  and  $C(11)$  chains running parallel to the  $b$  axis. The combination of these chains generates a chain of edge-fused  $R_4^+(40)$  rings parallel to the  $ab$  plane (Fig. 2).

Fig. 3 shows two intermolecular  $\pi$ – $\pi$  interactions between the two symmetry-related pyridine rings within the complex (I). Ring 3, defined by atoms N1/C1/C2/C3/C4/C5, has a perpendicular distance to its symmetry-related counterpart of 3.979 Å; the distance between the ring centroids Cg3 and Cg3<sup>i</sup> is 3.981 (2) Å. Ring 4, defined by atoms N2/C7/C8/C9/C10/C11, has a perpendicular distance to its symmetry-related counterpart of 3.558 Å; the distance between the ring centroids Cg4 and Cg4<sup>i</sup> is 3.658 (2) Å.

## Experimental

The title  $[\text{Cd}(\text{acs})_2(\text{H}_2\text{O})_4]$  complex was synthesized as reported previously (İçbudak *et al.*, 2006).  $[\text{Cd}(\text{acs})_2(\text{H}_2\text{O})_4]$  (0.5 mmol) was dissolved in acetone (50 ml) and a solution of 3-methylpyridine (1 mmol) in acetone (50 ml) was added to the stirred solution, which was stirred vigorously for 3 h at 323 K and then cooled to ambient temperature. The resulting colourless crystals were washed with acetone–1,2-dichloroethane (1:1 *v/v*) and dried under vacuum (yield 92%).

## Crystal data

$[\text{Cd}_2(\text{C}_4\text{H}_4\text{NO}_4\text{S})_2(\text{C}_6\text{H}_7\text{N})_2]$	$V = 5009.0 (7) \text{ \AA}^3$
$M_r = 1245.87$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.9475 (12) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$b = 16.5004 (11) \text{ \AA}$	$T = 296 \text{ K}$
$c = 21.4067 (15) \text{ \AA}$	$0.47 \times 0.43 \times 0.28 \text{ mm}$
$\beta = 108.427 (6)^\circ$	

## Data collection

Stoe IPDS-II diffractometer	13627 measured reflections
Absorption correction: integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)	4901 independent reflections
$T_{\min} = 0.637$ , $T_{\max} = 0.763$	3749 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	319 parameters
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
4901 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cd1—N1	2.286 (3)	S1—O1	1.418 (3)
Cd1—N2	2.285 (3)	S1—O2	1.409 (3)
Cd1—N3	2.526 (2)	S1—O3	1.617 (2)
Cd1—N4	2.434 (2)	S2—O6	1.396 (3)
Cd1—O4	2.380 (3)	S2—O7	1.412 (3)
Cd1—O5 <sup>i</sup>	2.384 (2)	S2—O8	1.609 (2)
Cd1—O5	2.560 (2)	O4—C13	1.244 (4)
S1—N3	1.577 (3)	O5—C17	1.254 (3)
S2—N4	1.581 (2)		
N1—Cd1—N2	168.93 (8)	N3—Cd1—O5	167.60 (8)
N1—Cd1—N3	87.31 (9)	O4—Cd1—N4	87.06 (8)
N1—Cd1—N4	91.55 (9)	O5 <sup>i</sup> —Cd1—N3	97.76 (8)
N1—Cd1—O5	90.29 (8)	O5 <sup>i</sup> —Cd1—O5	69.90 (7)
N1—Cd1—O5 <sup>i</sup>	85.22 (8)	O2—S1—O1	117.2 (2)
N2—Cd1—N3	90.39 (9)	O6—S2—O7	118.7 (2)
N2—Cd1—N4	97.14 (9)	C17—O5—Cd1	93.93 (18)
N2—Cd1—O5 <sup>i</sup>	84.36 (9)	Cd1 <sup>i</sup> —O5—Cd1	110.04 (7)
N2—Cd1—O5	89.64 (8)		

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

All H atoms were positioned geometrically and refined with a riding model, fixing the bond lengths at 0.93 and 0.96  $\text{\AA}$  for CH and  $\text{CH}_3$  groups, respectively. The  $U_{\text{iso}}(\text{H})$  values were constrained to be  $1.2U_{\text{eq}}(\text{parent})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ .

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s)

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C18—H18 $\cdots$ O1 <sup>i</sup>	0.93	2.58	3.419 (4)	150
C6—H6C $\cdots$ O6 <sup>ii</sup>	0.96	2.55	3.413 (5)	150

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

used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3020). Services for accessing these data are described at the back of the journal.

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