

Bis(acesulfamato)tetraaquacobalt(II)

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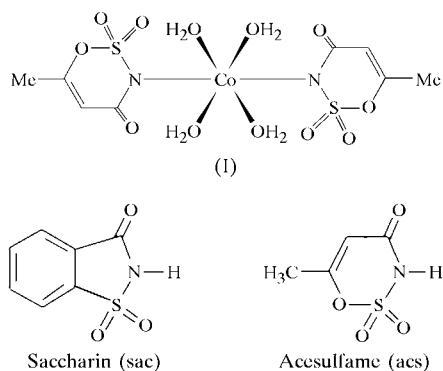
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The crystal structure of the first acesulfame–metal complex, namely tetraaquabis[6-methyl-1,2,3-oxathiazin-4(3*H*)-onate 2,2-dioxide- κ N]cobalt(II), [Co(C₄H₄NO₄S)₂(H₂O)₄], is reported. The Co^{II} ion resides on a twofold axis and is coordinated by four aqua ligands defining the basal plane and by two monodentate acesulfamate ligands, *via* their ring N atoms, in the axial positions. Two intra- and three intermolecular hydrogen-bonding interactions stabilize the crystal structure and form an infinite three-dimensional lattice.

Comment

Acesulfame (C₄H₅SO₄N) 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 the chemist Karl Clauss in 1967 (Clauss & Jensen, 1973) and has been widely used as a non-calorific 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). Chemically, it bears some structural resemblance to saccharin (see scheme above).

The acesulfamate anion (acs), C₄H₄NO₄S[−], has several potential donor atoms and thus, as a polyfunctional ligand, it can engage in N, O_{CO}, O_{OSO} or O coordination with different metal ions, similar to the saccharinate anion (sac). The chemistry of metal–artificial sweetener complexes is an interesting area of research because of the potential biological significance of such compounds; the structural literature on metal saccharinates reveals a large number of coordinated saccharinate residues (Haider *et al.*, 1985; İcbudak *et al.*, 2002, 2003; Naumov *et al.*, 2001; Deng *et al.*, 2001; Quinzani *et al.*, 2002; Yilmaz *et al.*, 2004). The present work describes the crystal structure of the title compound, *trans*-bis(acesulfamato)tetraaquacobalt(II), (I). This complex is the first reported example of a complex containing the acesulfamate ligand among several new complexes synthesized in this laboratory.

A view of the molecule of (I) with the atom-numbering scheme is shown in Fig. 1. In the structure, the Co^{II} ion resides on a twofold axis, coordinated by four aqua ligands defining the basal plane and by two monodentate acesulfamate ligands, *via* their ring N atoms, occupying the axial positions. The acesulfamate ligands in the structure are mutually *trans*, with their sulfonyl groups *trans* to each other. The bond lengths and angles of the metal-bonded acesulfamate ligands show some differences from the analogous potassium salt (Paulus, 1975). The most pronounced of these is the S1–N1–C1 bond angle, which is reduced to 117.65 (16)° in (I), from the corresponding value of 122.9 (2)° in the potassium salt. This obviously originates from the metal coordination of the N atom of the acesulfamate ligand. A significant deviation of −0.2430 (10) Å for atom S1 from the least-squares plane of the acesulfame ring (N1/C1–C3/O2/S1) is also observed.

From inspection of the metal–ligand bond distances in Table 1, it can be seen that the Co–N bond is longer than the Co–O bond, indicating that the Co–N bond is not very strong. This is to be expected if one considers the delocalization of negative charge away from the N atom in the ring. The negative charge is mainly localized on the sulfonyl and ring O atoms, if one compares the N1–S1 [1.5887 (18) Å] and S1–O2 [1.5987 (18) Å] bond distances with the corresponding values (1.544 and 1.624 Å, respectively) found in the potassium acesulfame salt.

The local structure around the Co^{II} ion in (I), [Co(acs)₂(H₂O)₄], can be compared with that in [Co(sac)₂]

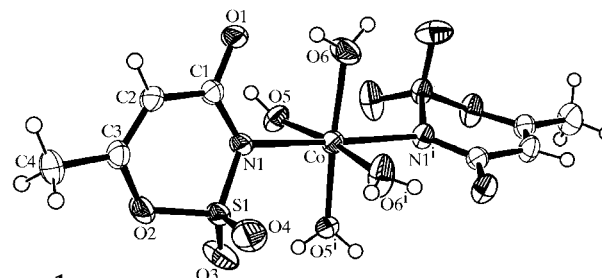


Figure 1

A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) 1 − *x*, *y*, $\frac{1}{2}$ − *z*.]

(H₂O)₄·2H₂O (Haider *et al.*, 1983), since both ligands have a structural resemblance, as shown in the scheme. Thus, one can observe that the Co—N_{acs} distance of 2.3180 (19) Å in (I) is longer than the Co—N_{sac} distance of 2.200 (1) Å in [Co(sac)₂(H₂O)₄]·2H₂O, while the two Co—O_{aqua} distances of 2.0338 (19) and 2.0567 (18) Å in (I) are shorter than the Co—O_{aqua} bonds of 2.060 (1) and 2.124 (2) Å in [Co(sac)₂(H₂O)₄]·2H₂O. The angular distortions of the octahedral environment of the Co^{II} ion in (I) also show some differences from those in the [Co(sac)₂(H₂O)₄]·2H₂O complex. The maximum deviation from an ideal O—M—O/N angle of 90° is 8.74 (9)° for (I), while it is only 2.8° for the saccharin complex.

With regard to the ligand geometry, the C—O bond length of the carbonyl group is increased by 0.012 Å in (I) compared with the potassium salt, whereas no significant changes are observed for the sulfonyl group. The bond lengths of these groups are especially important for IR studies, from which the coordination behaviour of the ligand (Grupce *et al.*, 2001; Naumov *et al.*, 2001) can be estimated.

The H atoms of the H₂O ligands are involved in both intra- and intermolecular hydrogen bonds with the carbonyl and sulfonyl O atoms of the acs ligand. The intramolecular O6—H6A···O1 and O5—H5B···O4(*x* + ½, *y* - ½, *z*) hydrogen bonds have H···O distances of 1.85 (4) and 2.38 (3) Å, respectively. These values indicate that the former interaction, between the H atom of one aqua ligand and the carbonyl O atom, is very strong when compared with that between the other aqua H atom and the sulfonyl O atom. This is due to the fact that the carbonyl group is a more basic site than the sulfonyl group.

When the hydrogen-bond regime of the carbonyl O atom of (I) is compared with that for the same group of the cobalt-saccharin complex, it can be seen that they both have one intra- and one intermolecular hydrogen bond. Nevertheless, the O6—H6A···O1 hydrogen bond [1.85 (4) Å] of the acesulfame complex is stronger than the corresponding bond in the saccharin complex (1.98 Å), while the O5—H5A···O1

hydrogen bond [1.94 (2) Å] is almost same as the corresponding bond in the saccharin complex (1.94 Å). This difference might originate from the difference in the chemical environments of the donors, where both donors for the acesulfame complex are aqua ligands, while the donors are an aqua ligand and a solvate water molecule in the saccharin complex. There are also three intermolecular hydrogen-bonding interactions in the structure of (I), as given in Table 2, which stabilize the crystal structure and form an infinite three-dimensional lattice.

Experimental

A solution of acesulfame potassium salt (0.41 g, 2 mmol) in distilled water (50 ml) was added dropwise with stirring to a hot solution of cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) in ethanol (50 ml). The mixture was stirred at 353 K for 2 h and then evaporated to dryness in a temperature-controlled bath at 353 K. The complex which formed was separated from the KClO₄ by extraction with absolute ethanol and was recrystallized from a solution in ethanol-acetone (1:1). The pink crystals of (I) which formed were filtered off, washed with acetone and dried *in vacuo*.

Crystal data

[Co(C₄H₄NO₄S)₂(H₂O)₄]
M_r = 455.28
 Monoclinic, *C2/c*
a = 13.2321 (14) Å
b = 8.9874 (6) Å
c = 13.9519 (15) Å
 β = 103.854 (8)°
V = 1610.9 (3) Å³
Z = 4

D_x = 1.877 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 9609 reflections
 θ = 2.8–25.9°
 μ = 1.39 mm⁻¹
T = 293 (2) K
 Prismatic, pink
 0.37 × 0.25 × 0.19 mm

Data collection

Stoe IPDS-2 diffractometer
 ω scans
 Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.516, *T_{max}* = 0.736
 9404 measured reflections

1548 independent reflections
 1249 reflections with *I* > 2σ(*I*)
R_{int} = 0.072
 θ_{max} = 25.8°
h = -16 → 16
k = -10 → 10
l = -16 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.028
wR(*F*²) = 0.068
S = 0.95
 1548 reflections
 132 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0411*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.53 e Å⁻³
 Δρ_{min} = -0.47 e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0063 (5)

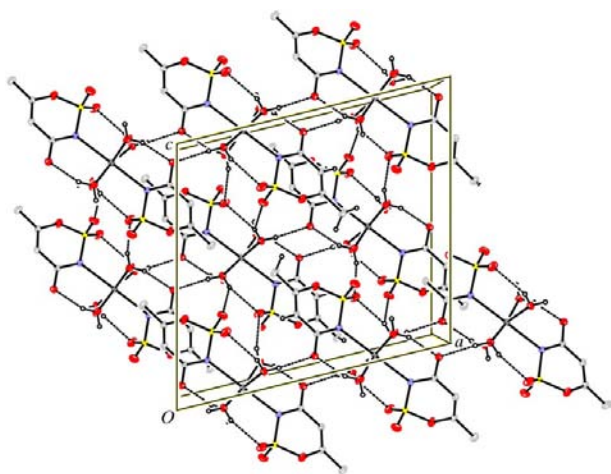


Figure 2

A view of the structure of (I) along the *b* direction, shown with 10% probability displacement ellipsoids. Dashed lines illustrate the hydrogen bonds. Carbon-bound H atoms have been omitted for clarity.

Table 1

Selected geometric parameters (Å, °).

Cl—O1	1.251 (3)	O2—S1	1.5987 (18)
Cl—N1	1.361 (3)	O3—S1	1.4188 (18)
Cl—C2	1.450 (3)	O4—S1	1.409 (2)
C2—C3	1.315 (3)	O5—Co1	2.0567 (18)
N1—S1	1.5887 (18)	O6—Co1	2.0338 (19)
N1—Co1	2.3180 (19)		
C1—N1—S1	117.65 (16)	O6—Co1—N1 ⁱ	87.83 (8)
O6 ⁱ —Co1—O6	92.60 (14)	O6—Co1—N1	88.95 (8)
O6—Co1—O5	92.12 (9)	O5 ⁱ —Co1—N1	98.80 (7)
O5 ⁱ —Co1—O5	84.25 (10)	O5—Co1—N1	84.69 (7)

Symmetry code: (i) 1 - *x*, *y*, ½ - *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots O1 ⁱⁱ	0.79 (2)	1.94 (2)	2.719 (2)	175 (4)
O5—H5B \cdots O3 ⁱⁱⁱ	0.81 (3)	2.14 (3)	2.780 (3)	136 (3)
O5—H5B \cdots O4 ^{iv}	0.81 (3)	2.38 (3)	3.051 (3)	141 (3)
O6—H6A \cdots O1	0.78 (3)	1.85 (4)	2.589 (3)	160 (3)
O6—H6B \cdots O3 ⁱ	0.79 (4)	2.18 (4)	2.912 (3)	156 (4)

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

The H atom on the ring C atom was placed in a calculated position, with C—H = 0.93 Å, and allowed to ride on its parent atom, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The methyl H atoms were placed as an idealized methyl group, with C—H = 0.96 Å and torsion angles from the electron-density map, and allowed to ride on the parent atom, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. All other H atoms were placed from the difference map and were included in the refinement with O—H distances restrained to 0.82 (2) Å. The maximum and minimum electron-density peaks were located 0.94 and 0.86 Å from atoms O2 and Co1, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Burnett & Johnson, 1996); 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: SK1780). Services for accessing these data are described at the back of the journal.

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