

## Bis(acesulfamato- $\kappa^2N^3, O^4$ )bis(2-aminopyrimidine- $\kappa N^1$ )copper(II)

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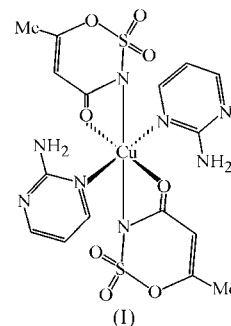
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In the crystal structure of the title compound, bis(2-aminopyrimidine- $\kappa N^1$ )bis[6-methyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide(1-)- $\kappa^2N^3, O^4$ ]copper(II), [Cu(C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S)<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>], the first mixed-ligand complex of acesulfame, the Cu<sup>II</sup> centre resides on a centre of symmetry and has an octahedral geometry that is distorted both by the presence of four-membered chelate rings and by the Jahn–Teller effect. The equatorial plane is formed by the N atoms of two aminopyrimidine (ampym) ligands and by the weakly basic carbonyl O atoms of the acesulfamate ligands, while the more basic deprotonated N atoms of these ligands are in the elongated axial positions with a strong misdirected valence. The crystal is stabilized by pyrimidine ring stacking and by intermolecular hydrogen bonding involving the NH<sub>2</sub> moiety of the ampym ligand and the carbonyl O atom of the acesulfamate moiety.

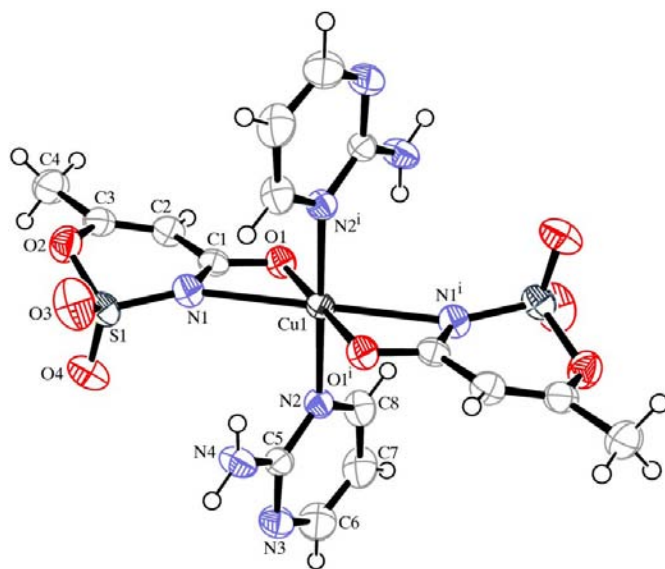
### Comment

The chemistry of the common artificial sweetener acesulfame (acs) is of interest not only because of its biological importance but also because of its coordination properties, since the acesulfame anion (acs<sup>-</sup>) offers different donor atoms to metal centres, namely ring N, carbonyl O, ring O and two sulfonyl O atoms. Despite its potential for diversity in coordination, little has been reported on the coordination behaviour of acesulfamate as a ligand. Recently, we have started to study the synthesis and the spectroscopic and structural properties of acesulfamate metal complexes (İçbudak, Heren *et al.*, 2005; İçbudak, Bulut *et al.*, 2005). The donor sites of the acesulfamate ligand are similar to those of the saccharinate anion, and therefore the coordination behaviour of the title compound, (I), can be compared with the coordination chemistry of saccharine, since all possible bonding patterns of saccharine are well documented by X-ray diffraction studies (İçbudak *et al.*, 2002, and references therein). As part of our ongoing

research on the coordination behaviour of acesulfame in transition metal complexes, complex (I) has been synthesized and its crystal structure determined.



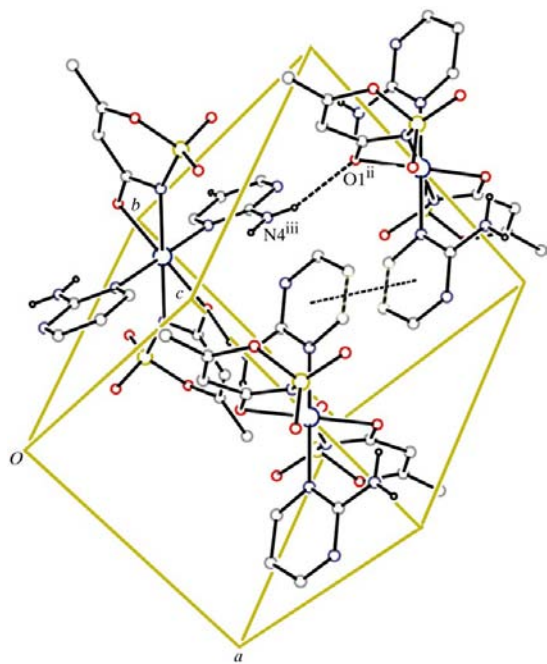
The molecular structure and atom-labelling scheme are shown in Fig. 1. The structure is composed of discrete [Cu(acs)<sub>2</sub>(ampym)<sub>2</sub>] molecules. The copper centre is bonded to two pyrimidine N atoms and two bidentate acesulfamate ligands chelated through the carbonyl O and the N atom. The geometry around the copper(II) ion (Table 1) is that of a distorted octahedron, of which the equatorial plane (N2/O1/N2<sup>i</sup>/O1<sup>i</sup>) is formed by two N atoms of two *trans* ampym ligands (N2 and N2<sup>i</sup>) and two carbonyl O atoms of two *trans*-oriented acesulfamate ligands (O1 and O1<sup>i</sup>) [symmetry code: (i) 1 - x, -y, -z]. The axial positions in the octahedron are occupied by two N atoms of acesulfamate ligands (N1 and N1<sup>i</sup>). The significant difference between the Cu–L bond distances [Cu–O1/O1<sup>i</sup> = 2.0107 (13) Å and Cu–N2/N2<sup>i</sup> = 2.0046 (16) Å] in the equatorial plane and the Cu–L distances [Cu–N1/N1<sup>i</sup> = 2.4597 (16) Å] in the axial positions has also been observed in other chelated copper complexes (Sieroń & Bukowska-Strzyzewska, 1997, and references therein; Albada *et al.*, 2002). Sieroń & Bukowska-Strzyzewska (1997) also established a correlation between equatorial Cu–



**Figure 1**  
 An ORTEP (Burnett & Johnson, 1996) view of the title molecule, with atoms shown as 50% probability displacement ellipsoids. [Symmetry code: (i) 1 - x, -y, -z.]

*L* bond lengths and the average axial Cu–*L* distances in the mixed-ligand complexes of copper pyridine-2-carboxamide. The correlation clearly indicated that the Cu–*L* distance in the equatorial plane is inversely proportional to the axial Cu–*L* distance. This result can easily be explained if one considers the Jahn–Teller distortion observed in most octahedral copper(II) complexes. The displacement parameters for N1 and O1 suggest a slight dynamic component to the Jahn–Teller effect, as the values of  $\Delta(\text{MSDA})$  (MSDA is mean-square displacement amplitude; Hirshfeld, 1976) for the Cu1–N1 and Cu1–O1 bonds are 0.0047 (9) and 0.0046 (7) Å<sup>2</sup>, respectively, values which are significantly larger than those for all of the other bonds in the structure. We note here also that the Cu1–N1 bond is significantly bent; the misdirected valence, defined as the angle between the Cu1–N1 vector and the external bisector of the C1–N1–S1 angle, has a value of 41.8°. The acute angle [58.79 (5)°] of the acesulfamate ligand is comparable to the related bite angle of 56.96° in the bis(2-aminopyrimidine)bis(nitrato)copper(II) complex (Albada *et al.*, 2002) and is slightly larger than that in bis(nicotinamide)bis(salicylato)copper(II) [52.72 (7)°; Leban *et al.*, 1997].

With regard to the acesulfamate ligand, the metal coordination of the carbonyl O atom affects the C–O bond length [1.274 (2) Å], which is greater than the related bond length in [Co(acs)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (İçbudak, Bulut *et al.*, 2005) and in the potassium salt of acs (Paulus, 1975). Some changes were also observed in the ring angles, and the maximum deviation from the values for the potassium salt is 3.6°, observed for the O2–S1–N1 angle. This change probably originates from the bidentate coordination behaviour of the acesulfamate ligand.



**Figure 2**  
The three-dimensional structure of the neutral title complex. Dashed lines illustrate the  $\pi$ – $\pi$  and hydrogen-bond interactions. H atoms, except for the amino H atoms, have been omitted for clarity. [Symmetry codes: (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .]

The 2-aminopyrimidine ligands are almost planar. Their individual bond lengths do not depart significantly from their respective mean values and correspond well to those reported for this ligand in other complexes (Albada *et al.*, 2004; Altin *et al.*, 2004; Prince *et al.*, 2003; Masaki *et al.*, 2002).

Because the acesulfamate and saccharinate ligands are similar in terms of donor sites, we can compare the metal coordination of acesulfamate with related saccharinate complexes. From that point of view, an N···O<sub>CO</sub> chelate of acesulfamate is very interesting, since this behaviour is only observed in cases of high metal coordination numbers for saccharinate complexes and was only suggested for large ionic radii in rare-earth complexes, *e.g.* europium(III) (Zheng, 1996). This mode has also been exclusively reported in the structure of lead(II) saccharinate, which has N and carbonyl O atoms from the same saccharinate ion coordinated to the same lead(II) cation. These studies for metal saccharine led to a conclusion that the chelating behaviour can only be observed for heavy metals, not for lighter ones (Baran *et al.*, 2000). The strong Cu–O interaction observed in this study is interesting because *M*–N is the most common coordination mode in transition metal complexes of saccharine. It is also known that *M*–O coordination only predominates in the case of alkaline and alkaline-earth saccharinates (Falvello *et al.*, 2001; Baran *et al.*, 2000; Haider *et al.*, 1983).

The crystal structure of (I) (Fig. 2) is stabilized by stacking of the pyrimidine rings. The centroid–centroid separation of the ring at (*x*, *y*, *z*) and that at ( $1 - x, -1 - y, -z$ ) is 3.950 Å and the vertical separation of these parallel ring planes is 3.554 Å. There is also a hydrogen-bonding interaction between atom H4D of the amine group and the carbonyl O atom of a neighbouring molecule [H4D···O1 = 2.25 Å, N4–H4D···O1 = 162° and N4···O1 = 3.074 (2) Å].

## Experimental

[Cu(acs)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (0.460 g, 1 mmol) was dissolved in ethanol (30 ml) and 2-aminopyrimidine (0.190 g, 2 mmol, ampym) in ethanol (30 ml) was added to the stirred solution. The mixture was stirred at 323 K for a further 1 h and was then cooled to ambient temperature. The resulting blue crystals were washed with acetone and dried under vacuum (yield 93.00%).

### Crystal data

[Cu(C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S)<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 578.04  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 10.6129 (9) Å  
*b* = 8.9750 (5) Å  
*c* = 12.6808 (10) Å  
 $\beta$  = 113.227 (6)°  
*V* = 1109.96 (14) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.730 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 12 380 reflections  
 $\theta$  = 2.1–27.6°  
 $\mu$  = 1.24 mm<sup>−1</sup>  
*T* = 296 (2) K  
 Prism, blue  
 0.54 × 0.47 × 0.20 mm

### Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: integration  
 (*X-RED32*; Stoe & Cie, 2002)  
 $T_{\min}$  = 0.467,  $T_{\max}$  = 0.582  
 16 919 measured reflections  
 2458 independent reflections

2345 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.121  
 $\theta_{\text{max}}$  = 27.3°  
 $h$  = −13 → 13  
 $k$  = −11 → 11  
 $l$  = −16 → 16

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.116$   
 $S = 1.22$   
 2458 reflections  
 161 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.1622P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.27 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$

**Table 1**

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

C1—O1	1.274 (2)	Cu1—O1	2.0107 (13)
C1—N1	1.333 (3)	Cu1—N1	2.4597 (16)
Cu1—N2	2.0046 (16)	N1—S1	1.5876 (17)
O1—Cu1—N1	58.79 (5)	N1—S1—O2	104.63 (9)

The methyl H atoms were placed at idealized positions (C—H = 0.96  $\text{\AA}$ ), with the torsion angles established from a difference map, and were allowed to ride on the parent atom [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ]. The other H atoms were placed at calculated positions (C—H = 0.93  $\text{\AA}$  and N—H = 0.85  $\text{\AA}$ ) and were allowed to ride on the parent atom [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ ]. The highest peak in the electron-density difference map is 0.90  $\text{\AA}$  from atom Cu1.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (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: FA1117). Services for accessing these data are described at the back of the journal.

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