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

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In the crystal structure of the title compound {systematic name: bis[6-methyl-1,2,3-oxathiazin-4(3H)-one 2,2-dioxide-(1−)-$\kappa^2N^3,O^4$]bis(3-methylpyridine)copper(II)}, [Cu(C₄H₄-NO₄S)₂(C₆H₇N)₂], the Cu$^{II}$ 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 because of the Jahn–Teller effect. The equatorial plane is formed by the N atoms of two methylpyridine ligands and by the more basic O atoms of the acesulfamate ligands, while the weakly basic N atoms of these ligands are in elongated axial positions with a misdirected valence. The crystal is stabilized by two intermolecular C—H···O interactions involving the methyl and CH groups, and the sulfonyl O atoms of the acesulfamate group.

## 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 acesulfamate anion (acs⁻) 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; Bulut et al., 2005; İçbudak, Adıyaman et al., 2006). 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 saccharin, since all possible bonding patterns of saccharin are well documented by X-ray diffraction studies (İçbudak et al., 2002, and references therein). In order to examine the coordination behaviour of acesulfame in transition metal complexes, complex (I) has been synthesized and its crystal structure is presented here.

The molecular structure and atom-labelling scheme are shown in Fig. 1. The structure is composed of discrete



(I)
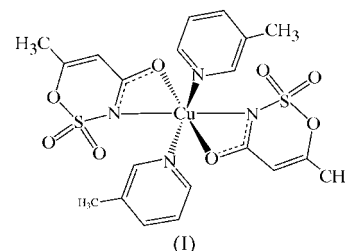
[Cu(acs)₂(mepyr)₂] molecules (mepyr is methylpyridine). The geometry around the copper(II) ion (Table 1) is that of a distorted octahedron, of which the equatorial plane (N2/O4/N2$^i$/O4$^i$) is formed by two N atoms of two trans pyridine ligands [N2 and N2$^i$; symmetry code: (i) −x + 1, −y, −z + 1] and two O atoms of two trans-oriented acesulfamate ligands (O4 and O4$^i$). The axial positions in the octahedron are occupied by two N atoms of acesulfamate ligands (N1 and N1$^i$). The significant difference between the Cu—$L_{eq}$ bond distances (Cu—O4/O4$^i$ and Cu—N2/N2$^i$) in the equatorial plane and the Cu—$L_{ax}$ distances (Cu—N1/N1$^i$) in the axial positions (Table 1) has also been observed in other chelated copper complexes (Sieroń & Bukowska-Strżyzewska, 1997, and references therein; van Albada et al., 2002; Vinogradova et al., 2002). Sieroń & Bukowska-Strżyzewska (1997) also established a correlation between equatorial Cu—$L_{eq}$ bond lengths and the average axial Cu—$L_{ax}$ distances in the mixed-ligand complexes of copper pyridine-2-carboxamide. The correlation clearly indicated that the Cu—$L_{eq}$ distance is inversely proportional to the axial Cu—$L_{ax}$ distance. This result can easily be explained if one considers the Jahn–Teller
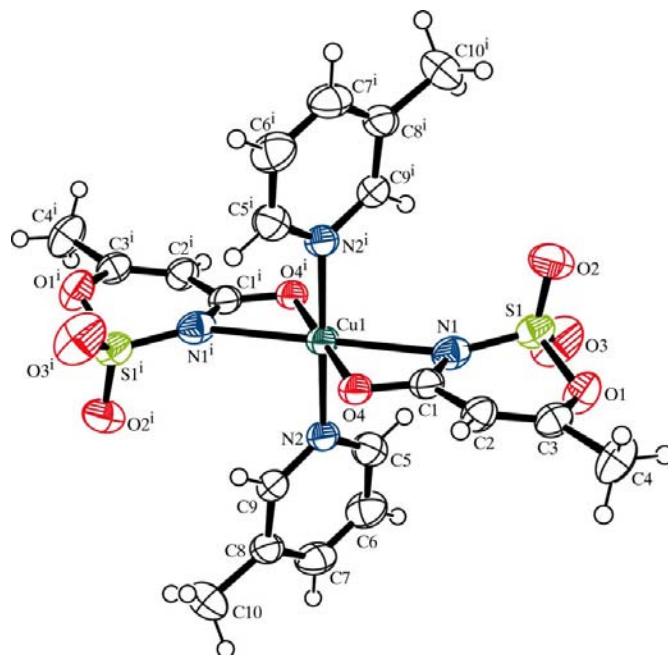


**Figure 1**
A view of the title molecule, with atoms shown as 50% probability displacement elipsoids. Only one set of the disordered methyl H atoms has been included. [Symmetry code: (i) 1 − x, −y, 1 − z.]

distortion observed in most octahedral copper(II) complexes. The displacement parameter for atom N1 suggests a slight dynamic component to the Jahn–Teller effect, as the value of $\Delta$(MSDA) [MSDA is mean-square displacement amplitude (Hirshfeld, 1976)] for the Cu1—N1 bond is 0.0116 (14) Å$^2$, a value that is 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 37.6°. The acute bite angle [59.36 (8)°] of the acesulfamate ligand is comparable to the related bite angle of 56.96° in the bis(2-aminopyrimidine)bis(nitrato)copper(II) complex (van Albada et al., 2002) and is slightly larger than that in bis(nicotin-amide)bis(salicylato)copper(II) [52.72 (7)°; Leban et al., 1997].

With regard to the acesulfamate ligand, the metal coordi-nation of the O atom affects the C—O bond length, which is greater than the related bond length in [Co(acs)$_2$(H$_2$O)$_4$] (İçbudak, Bulut et al., 2005) and in the potassium salt of acs (Paulus, 1975). It is evident from the Cu—O$_{eq}$ and Cu—N$_{ax}$ bond distances that the O atom is coordinated much more strongly than the N atom. This suggests that the O atom is a better donor than the N atom, perhaps because it is more electronegative in the N—C—O link, showing a partial multiple-bond character. Some changes were also observed in the ring angles, and the maximum deviation from the values for the potassium salt is 3.4°, observed for the O1—S1—N1 angle. This change probably originates from the bidentate coordination behaviour of the acesulfamate ligand. The acesulfame ring adopts a half-chair conformation, as is evident from the puckering parameters [$Q = 0.365$ (2) Å, $\theta = 61.6$ (5)° and $\varphi = 6.902$ (14)° for the atom sequence S1—O1—C3—C2—C1—N1 (Cremer & Pople, 1975)]. The 3-methylpyridine ligands are 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 (Rotondo, 2006; Aygün et al., 2005; Goto et al., 2000; Naka-gawa et al., 2000).

Because the acesulfamate and saccharinate ligands are similar in terms of donor sites, we can compare the metal coordination of acesulfamate with that of related saccharinate complexes. From that point of view, an N···O$_{CO}$ 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 reported exclusively 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 saccharin 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 saccharin. 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).

In the crystal structure of (I), there are two intermolecular interactions of type C—H···O, which stabilize the crystal packing (Fig. 2 and Table 2). The first of these is between atom H4C of the methyl group of the acesulfamate ligand and a sulfonyl O atom of a neighbouring molecule. The second is between atom H2 of the acesulfamate ligand and a sulfonyl O atom of an adjacent molecule. There are no other significant interactions, such as $\pi$–$\pi$ and C—H···$\pi$ interactions, in the crystal structure of (I).

## Experimental

### Crystal data

| | |
|---|---|
| [Cu(C$_4$H$_4$O$_4$NS)$_2$(C$_6$H$_7$N)$_2$] | $Z = 2$ |
| $M_r = 574.08$ | $D_x = 1.601$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 10.7385$ (6) Å | $\mu = 1.15$ mm$^{-1}$ |
| $b = 9.1792$ (7) Å | $T = 296$ K |
| $c = 12.5005$ (8) Å | Prism, blue |
| $\beta = 104.892$ (5)° | $0.49 \times 0.43 \times 0.37$ mm |
| $V = 1190.80$ (14) Å$^3$ | |

### Data collection

| | |
|---|---|
| Stoe IPDS-II diffractometer | 18687 measured reflections |
| $\omega$ scans | 2736 independent reflections |
| Absorption correction: integration | 2395 reflections with $I > 2\sigma(I)$ |
| (X-RED32; Stoe & Cie, 2002) | $R_{int} = 0.046$ |
| $T_{min} = 0.581$, $T_{max} = 0.699$ | $\theta_{max} = 27.6°$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | $+ 2.0095P]$ |
| $wR(F^2) = 0.119$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.05$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 2736 reflections | $\Delta\rho_{max} = 0.92$ e Å$^{-3}$ |
| 155 parameters | $\Delta\rho_{min} = -1.29$ e Å$^{-3}$ |
| H-atom parameters constrained | |
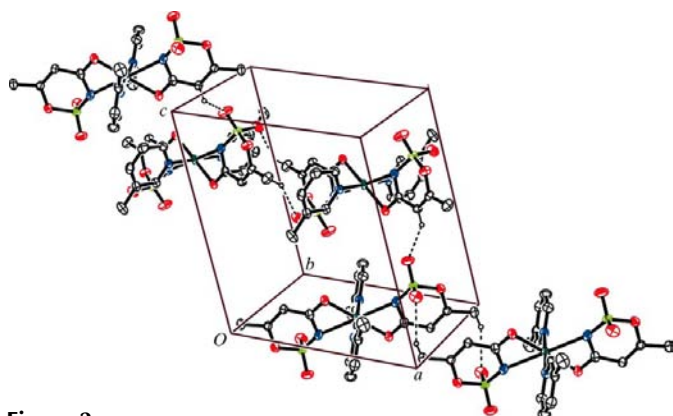


**Figure 2**
The hydrogen-bonding interactions (dashed lines) in the structure of (I), with atoms shown as 30% probability displacement elipsoids. For clarity, H atoms not involved in hydrogen bonding have been omitted.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N2 | 2.001 (2) | S1—N1 | 1.579 (3) |
| Cu1—O4 | 2.044 (2) | O4—C1 | 1.267 (4) |
| Cu1—N1 | 2.405 (3) | N1—C1 | 1.340 (4) |
| | | | |
| O4—Cu1—N1 | 59.36 (8) | C1—N1—S1 | 119.5 (2) |
| N1—S1—O1 | 104.84 (13) | C1—N1—Cu1 | 82.61 (18) |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| C4—H4$C$⋯O2$^i$ | 0.96 | 2.49 | 3.334 (5) | 146 |
| C2—H2⋯O3$^{ii}$ | 0.93 | 2.59 | 3.194 (4) | 123 |

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

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96 and 0.93 Å for methyl and aromatic H atoms, respectively. The displacement parameters of the H atoms were constrained as $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C)$ for methyl H atoms] of the parent atom. The H atoms of one of the methyl groups were found to be disordered over two positions and option AFIX 123 of *SHELXL97* (Sheldrick, 1997) was used.

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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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