# Bis(4-aminobenzenesulfonato-κN)bis(N,N-dimethylformamide-κO)copper(II)

**Yun-Long Fu,[a] Min-Na Sun,[a] Xiao-Fang Zhi[a] and Seik Weng Ng[b]***

[a]School of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The Cu atom in the title zwitterionic complex, [Cu(C$_6$H$_6$-N$_2$O$_3$S)$_2$(C$_3$H$_7$NO)$_2$], lies on a centre of inversion in a square plane formed by two N and two O atoms. Adjacent zwitterions are linked by a long Cu—O interaction of 2.465 (2) Å to form a linear chain that runs along the $b$ axis of the triclinic unit cell. The chain motif is consolidated by N—H···O hydrogen bonds.

## Comment

The 4-aminobenzoate anion can bind to transition metals through the amino as well as the carboxylate ends, as noted from the diaqua copper and manganese derivatives, [Cu(H$_2$NC$_6$H$_4$SO$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O and [Mn(H$_2$NC$_6$H$_4$SO$_3$)$_2$(H$_2$O)$_2$] (Gunderman *et al.*, 1996). In two further derivatives, the isostructural compounds [Co(H$_2$NC$_6$H$_4$SO$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O (Shakeri & Haussuhl, 1992*a*) and [Zn(H$_2$NC$_6$H$_4$SO$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O (Shakeri & Haussuhl, 1992*b*), both ends engage in coordination.



(I)
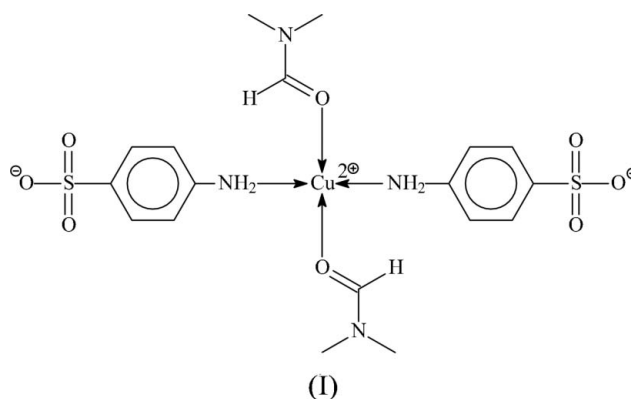
The reaction of the 4-aminobenzoate anion with copper(II) gives the title compound, (I), in which the anion coordinates through the amino group. The O atoms of two dimethylformamide (DMF) solvent molecules complete the centrosymmetric square-planar geometry. The geometry is distorted towards octahedral owing to the long copper–sulfonate bond (Table 1, Fig. 1). This bond gives rise to a linear chain, which is consolidated by intra-chain N—H···O hydrogen bonds. The binding mode of the anion in the present bis(DMF)–copper compound is similar to that found in the diaquacopper compound, whose geometry is tetragonally distorted from a square plane owing to a long Cu–O distance of 2.420 (2) Å (Gunderman *et al.*, 1996).

## Experimental

Copper(II) nitrate trihydrate (0.224 g, 1 mmol) was dissolved in excess dimethylformamide (5 ml) along with 4-aminobenzenesulfonic

acid (0.346 g, 2 mmol). The solution was heated at 343 K for 7 d. Green plate-shaped crystals of (I) were isolated from the cooled solution in an 80% yield based on Cu.

### Crystal data

| | |
|---|---|
| [Cu(C$_6$H$_6$N$_2$O$_3$S)$_2$(C$_3$H$_7$NO)$_2$] | $V = 556.09$ (7) Å$^3$ |
| $M_r = 554.09$ | $Z = 1$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.655$ Mg m$^{-3}$ |
| $a = 7.1168$ (5) Å | Mo $K\alpha$ radiation |
| $b = 8.4491$ (6) Å | $\mu = 1.22$ mm$^{-1}$ |
| $c = 9.5294$ (6) Å | $T = 295$ (2) K |
| $\alpha = 87.033$ (1)° | Plate, green |
| $\beta = 77.344$ (1)° | $0.20 \times 0.16 \times 0.04$ mm |
| $\gamma = 84.337$ (1)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEX area-detector diffractometer | 4574 measured reflections |
| $\varphi$ and $\omega$ scans | 2426 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 2246 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.797$, $T_{\max} = 0.953$ | $R_{\mathrm{int}} = 0.016$ |
| | $\theta_{\max} = 27.5°$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.4598P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.134$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| $S = 1.13$ | $\Delta\rho_{\max} = 0.43$ e Å$^{-3}$ |
| 2426 reflections | $\Delta\rho_{\min} = -0.40$ e Å$^{-3}$ |
| 161 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.047 (2) | Cu1—O4 | 1.994 (2) |
| Cu1—O1$^{\mathrm{ii}}$ | 2.465 (2) | | |
| O1$^{\mathrm{ii}}$—Cu1—O4 | 92.87 (8) | O1$^{\mathrm{ii}}$—Cu1—N1$^{\mathrm{i}}$ | 93.43 (8) |
| O1$^{\mathrm{ii}}$—Cu1—O4$^{\mathrm{i}}$ | 87.13 (8) | O4—Cu1—N1 | 86.64 (9) |
| O1$^{\mathrm{ii}}$—Cu1—N1 | 86.57 (9) | O4—Cu1—N1$^{\mathrm{i}}$ | 93.36 (9) |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y + 1, z$.

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H2n$\cdots$O2$^{\mathrm{ii}}$ | 0.85 (1) | 2.17 (1) | 3.018 (3) | 176 (3) |
| N1—H1n$\cdots$O2$^{\mathrm{iv}}$ | 0.85 (1) | 2.21 (2) | 2.987 (3) | 152 (4) |

Symmetry codes: (ii) $x, y + 1, z$; (iv) $-x + 2, -y, -z + 1$.

Carbon-bound H atoms were placed in calculated positions, with C—H = 0.93–0.96 Å, and were included in the refinement in the
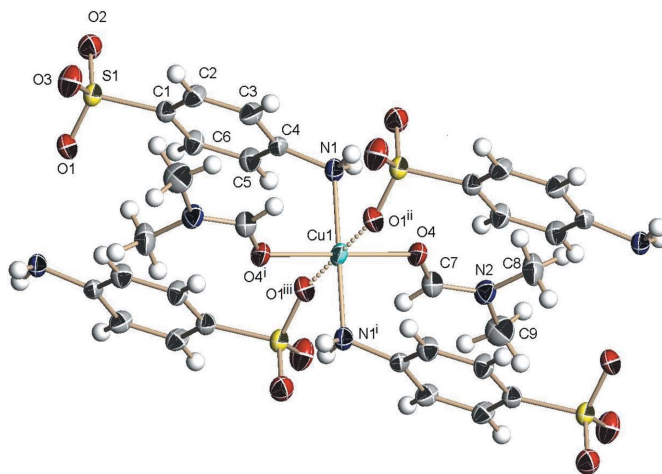


**Figure 1**
The coordination geometry of the Cu atom of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry codes are as in Table 1; additionally: (iii) $-x + 1, -y, -z + 1$.]

riding-model approximation, with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $1.5U_{\mathrm{eq}}(\mathrm{C}_{\mathrm{methyl}})$; the methyl groups were rotated to fit the electron density. The amino H atoms were located in a difference Fourier map, and refined with a distance restraint of N—H = 0.85 (1) Å; their displacement parameters were also refined.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

### References

Bruker (2003). SAINT (Version 6.36A) and SMART (Version 6.36A). Bruker AXS Inc., Madison, Winsonsin, USA.
Gunderman, B. J., Squattrito, P. J. & Dubey, S. N. (1996). Acta Cryst. C52, 1131–1134.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Shakeri, V. & Haussuhl, S. (1992a). Z. Kristallogr. 198, 165–166.
Shakeri, V. & Haussuhl, S. (1992b). Z. Kristallogr. 198, 167–168.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.