

## On the short carbonyl bond in bis[ $\mu$ -1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido- $\kappa^2$ N:O]bis[[1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido- $\kappa$ N]-bis(imidazole)copper(II)]

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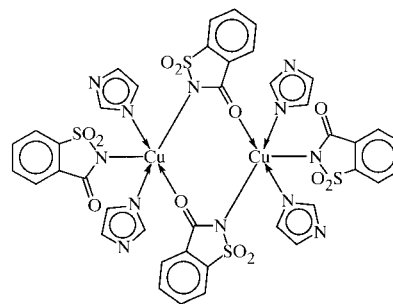
The short carbonyl bond in the title compound, [Cu<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>-NO<sub>3</sub>S)<sub>4</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>] [Liu, Huang, Li & Lin (1991). *Acta Cryst. C* **47**, 41–43], is an artifact of disorder in the isothiazol-3(2*H*)-one 1,1-dioxide part of the 1,2-benzisothiazol-3(2*H*)-one entity. In the present redetermination, all bond dimensions in the centrosymmetric dinuclear molecule are normal. The five-coordinate Cu atom shows trigonal-bipyramidal coordination. Hydrogen bonds from the imidazole donor ligand link adjacent molecules into a two-dimensional layer structure.

### Comment

The first-row transition metal derivatives of the artificial sweetener saccharin, 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide, are protease inhibitors (Supuran, 1993; Supuran *et al.*, 1993), and superoxide dismutase-like activity has been noted for these and other metal saccharinates (Apella *et al.*, 1993). Because imido, carbonyl and sulfonyl functionalities exist in the deprotonated saccharinate ion, the coordination chemistry of metal saccharinates is extremely rich and the crystallographic literature presents an extraordinary variety of bonding motifs. The bonding modes can also be conveniently assigned using vibrational spectroscopy. IR measurements have also aided in unravelling the factors that govern which of the competing vicinal groups will bind to the metal atom (Jovanovski *et al.*, 1990; Jovanovski & Šoptrajanov, 1988; Naumov & Jovanovski, 2000*a,b,c,d*, 2001*a,b*). Linking the vibrational spectral features with the X-ray results are the

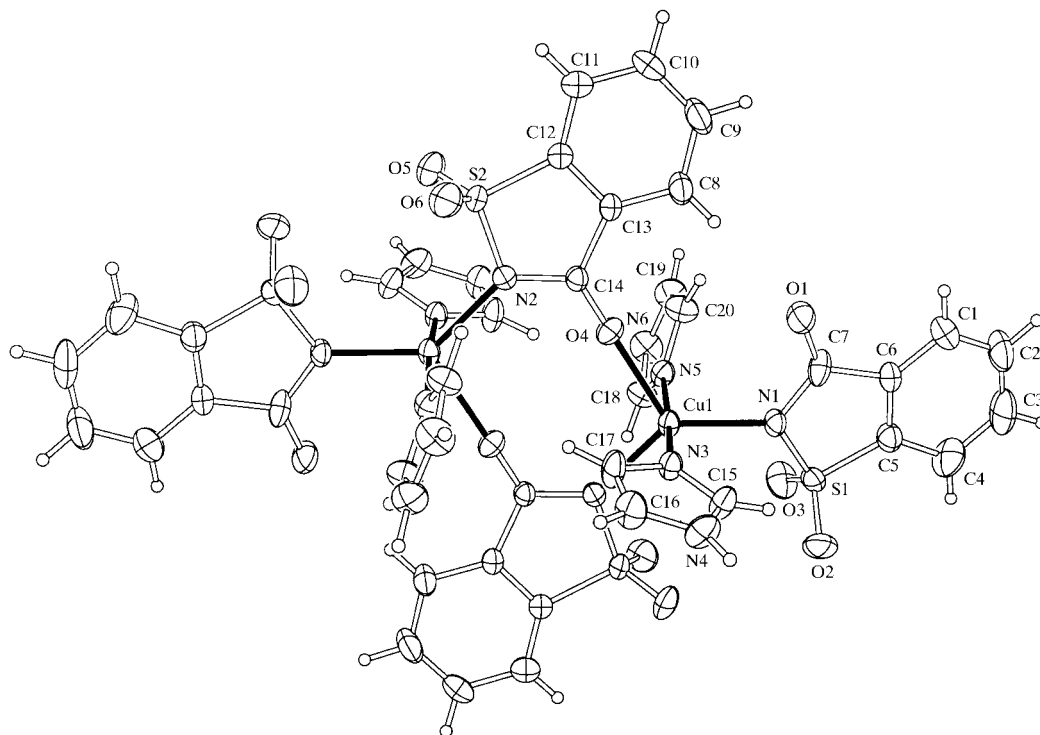
semi-empirical and Hartree–Fock/density functional theory (HF/DFT) *ab initio* force-field calculations (Binev *et al.*, 1996; Naumov & Jovanovski, 2000*b,c*); the calculations are particularly successful with systems such as the copper saccharinates (Naumov *et al.*, 2001).

Our interest in the title compound, (I), arose from the disagreement in one of the two carbonyl bond distances between the X-ray structure determined by Liu *et al.* (1991) [ $R = 0.049$  for 3275 reflections with  $I > 2\sigma(I)$ ] and the structure calculated from the IR and Raman spectra (Naumov & Jovanovski, 1999*a,b*; Naumov *et al.*, 2001). The distance in the bridging saccharinate group was normal [1.223 (5) Å], whereas that of the *N*-coordinated saccharinate was extremely short [1.103 (6) Å]. There were no other unusual features in the structure of (I), except for a somewhat long C–C distance and a somewhat short C–S distance in the latter group. The peculiarity was not commented on by Liu *et al.* (1991) in their study of (I), but the short carbonyl bond was later employed by others (Zhang *et al.*, 1995) to explain a ‘space obstacle’ effect arising from the neighboring imidazole ring. The distance is short in comparison with distances found in other saccharinates [mean C–O 1.23 (2) Å; Naumov & Jovanovski, 2000*a*] and is even shorter than some severely electronically-contracted carbonyl compounds, such as carbonyl difluoride [1.172 (1) Å] and carbonyl dichloride [1.176 (2) Å] (Kwiatkowski & Leszczynski, 1994). In fact, this bond would have a bond order (Paolini, 1990) of 2.75; however, a triple bond would not be possible owing to the nitranionic resonance structure. The short bond contrasts with the normal distance noted in the analogous cadmium complex (Li *et al.*, 1997). Under a more detailed analysis of the vibrational spectrum, the curve-fitted carbonyl stretching interval of the copper complex revealed a third, minor, Raman-active carbonyl component. Nevertheless, the spectrum presented convincing evidence for a normal length of 1.21–1.22 Å in all three carbonyl groups.

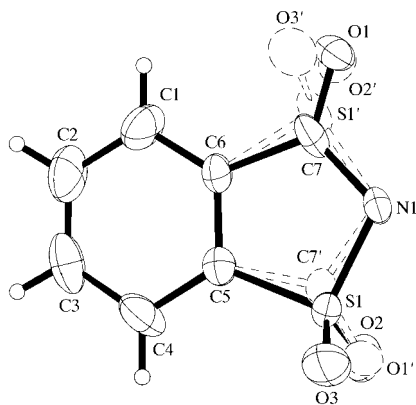


(I)

As steric effects alone cannot account for the short bond, we carried out a rerefinement from the deposited structure factors (supplementary publication No. SUP 52964). However, these calculations merely confirmed the apparent correctness of the original refinements. Nonetheless, we were still doubtful of the structure, hence the present measurements. In our re-examination, refinement on all reflections revealed the cause of the anomaly: the isothiazol-3(2*H*)-one 1,1-dioxide portion of the monodentate saccharinate entity is disordered across a

**Figure 1**

A view of the molecule of (I), with displacement ellipsoids at the 50% probability level and H atoms drawn as spheres of arbitrary radii.

**Figure 2**

ORTEP (Johnson, 1976) plot showing the disorder in the saccharinate group of (I); the benzothiazolyl planes are tilted by 8 (1)°.

pseudo-mirror plane, the ratio of the two forms being 7:1. Fig. 1 shows the structure; the minor component is not shown. One of the sulfonyl O atoms from the ordered saccharinate entity forms a strong hydrogen bond with the imidazole ring of an adjacent molecule [N...O 2.965 (4), H...O 2.15 (6) Å and N—H...O 171 (5)°].

The DFT calculations correctly model the isolated saccharinate ion (Fig. 2 and Table 3), whose carbonyl distance is 1.241 Å. When the anion is coordinated to a metal atom through its N atom, this bond contracts in the crystal structures (Naumov & Jovanovski, 2000a). Several restricted optimizations from modeled or previously optimized input with the anomalous parameter set to 1.103 Å, when tested on

various basis sets, led either to divergence (correlated methods) or to unrealistic local minima and loss of the planarity of the *o*-phenylene ring (Hartree–Fock methods). The theoretical results unambiguously rule out the possibility of a stable ground-state planar saccharinate species having the short carbonyl bond length.

In contrast with the plethora of wrong spectroscopic assignments that have later been corrected by crystallographic analyses, this re-investigation represents an unusual case of a crystal structure revision that was initiated by spectroscopic assignments.

## Experimental

Tetraaquabis(saccharinato)copper dihydrate was synthesized from copper(II) nitrate and sodium saccharinate in water. Lilac-colored crystals of (I) were grown from an aqueous mixture of the copper complex and imidazole in a 1:2 molar ratio. Elemental (C, H, N, S) analysis, <sup>1</sup>H NMR and UV–vis spectroscopic measurements, and thermal analyses, all confirmed the composition as [Cu<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>NO<sub>3</sub>S)<sub>4</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]. For the DFT quantum-chemical calculations, the global minimum of an isolated saccharinate ion in its ground electronic state was located using a stepwise unrestricted optimization procedure in which the energy derivatives up to the B3LYP/6-31++G(*d,p*) level (Becke, 1993) were computed analytically with the GAUSSIAN98 program suite (Frisch *et al.*, 1998) running on an ORIGIN2000 supercomputer. Harmonic vibrational analysis at the same level confirmed that the stationary point represented a minimum. The computations were repeated with the deviant C—O distance frozen at 1.103 Å, which is the distance given in the earlier report (Liu *et al.*, 1991).

## Crystal data

$[\text{Cu}_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_4(\text{C}_3\text{H}_4\text{N}_2)_4]$	$D_x = 1.717 \text{ Mg m}^{-3}$
$M_r = 1128.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8192 reflections
$a = 11.1176 (1) \text{ \AA}$	$\theta = 2.1\text{--}28.3^\circ$
$b = 11.5112 (1) \text{ \AA}$	$\mu = 1.25 \text{ mm}^{-1}$
$c = 17.1203 (1) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 95.346 (1)^\circ$	Parallelepiped, blue
$V = 2181.47 (3) \text{ \AA}^3$	$0.44 \times 0.36 \times 0.24 \text{ mm}$
$Z = 2$	

## Data collection

Siemens SMART CCD area-detector diffractometer	5330 independent reflections
$\omega$ scans	4073 reflections with $I > 2\sigma(I)$
Absorption correction: empirical ( <i>SADABS</i> ; Sheldrick, 1996)	$R_{\text{int}} = 0.068$
$T_{\text{min}} = 0.610$ , $T_{\text{max}} = 0.754$	$\theta_{\text{max}} = 28.3^\circ$
15 502 measured reflections	$h = -14 \rightarrow 14$
	$k = -13 \rightarrow 15$
	$l = -16 \rightarrow 22$

## Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2]$
$wR(F^2) = 0.139$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} < 0.001$
5330 reflections	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
332 parameters	$\Delta\rho_{\text{min}} = -1.24 \text{ e \AA}^{-3}$

**Table 1**

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

Cu1—N1	2.065 (2)	Cu1—N5	1.960 (2)
Cu1—N2 <sup>i</sup>	2.111 (2)	Cu1—O4	2.275 (2)
Cu1—N3	1.967 (2)		
N1—Cu1—N2 <sup>i</sup>	133.0 (1)	N2—Cu1—N5 <sup>i</sup>	92.7 (1)
N1—Cu1—N3	93.5 (1)	N2 <sup>i</sup> —Cu1—O4	105.6 (1)
N1—Cu1—N5	89.6 (1)	N3—Cu1—N5	172.0 (1)
N1—Cu1—O4	121.4 (1)	N3—Cu1—O4	87.1 (1)
N2—Cu1—N3 <sup>i</sup>	90.6 (1)	N5—Cu1—O4	85.0 (1)

Symmetry code: (i)  $-x, -y, -z$ .

**Table 2**

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N4—H4N <sup>i</sup> ···O2 <sup>i</sup>	0.86	2.45	2.913 (4)	114
N4—H4N <sup>i</sup> ···O5 <sup>ii</sup>	0.86	2.15	2.966 (4)	158
N6—H6N <sup>i</sup> ···O6 <sup>iii</sup>	0.86	2.43	2.965 (4)	121
N6—H6N <sup>i</sup> ···O2 <sup>iv</sup>	0.86	2.63	3.261 (4)	131
N6—H6N <sup>i</sup> ···O3 <sup>iv</sup>	0.86	2.43	3.036 (4)	128
N6—H6N <sup>i</sup> ···O1 <sup>iv</sup>	0.86	2.27	2.98 (2)	140

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

One of the two 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide ligands is disordered in the sulfonyl ( $\text{SO}_2$ ) and carbonyl ( $\text{CO}$ ) groups; the ratio of the occupancy of the major (unprimed) to the minor (primed) components refined to 7:1. The sulfonyl and carbonyl groups are disordered across a pseudo-mirror plane. A number of restraints were applied to treat the disorder. The displacement parameters of atom S1 were set equal to those of atom C7' and those of atom S1' equal to those of atom C7. The displacement parameters of the unprimed O atoms were set equal to those of the primed O atoms.

**Table 3**

Equilibrium B3LYP/6-31++G(*d,p*) geometry for the isolated saccharinate ion ( $\text{\AA}$ ,  $^\circ$ ).

S1—O2	1.483	C1—C2	1.401
S1—O3	1.483	C2—C3	1.403
S1—N1	1.357	C3—C4	1.402
S1—C5	1.813	C4—C5	1.393
O1—C7	1.241	C5—C6	1.388
N1—C7	1.642	C6—C7	1.525
C6—C1	1.393		
S1—N1—C7	111.9	C3—C4—C5	117.4
S1—C5—C6	106.2	C4—C5—C6	122.6
N1—S1—C5	96.6	C5—C6—C7	112.1
N1—C7—C6	113.2	C5—C6—C1	120.1
C1—C2—C3	120.7	C6—C1—C2	118.5
C2—C3—C4	120.6		

1,2-Related and 1,3-related bond distances involving atoms S1, C7 and O1 were restrained to be equal to those of the corresponding primed atoms by *SADI* 0.005 and *SADI* 0.010 instructions in *SHELXL97* (Sheldrick, 1997). A larger deviation in the *SADI* instructions gave somewhat unsatisfactory angles at the minor carbonyl C atom. The isothiazolyl C5—C6—C7(S1')—N1—S1(C7') unit (r.m.s. deviation 0.020  $\text{\AA}$ ) was restrained to be flat by a *FLAT* 0.01 instruction. The 1,2-phenylene ring (r.m.s. deviation 0.004  $\text{\AA}$ ) is coplanar with this unit [dihedral angle 2.5 (2) $^\circ$ ] and is not split into two components. H atoms were treated as riding, with C—H = 0.93  $\text{\AA}$  and N—H = 0.86  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H})$  equal to 1.2 times  $U_{\text{eq}}$  of the parent atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1032). Services for accessing these data are described at the back of the journal.

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