

Structure of a Copper Complex Containing Saccharin and Imidazole: [Cu₂(C₆H₄COSO₂N)₄(C₃H₄N₂)₄]

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Abstract. Bis[μ -1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido- κ N: κ O]bis[1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido- κ N]tetrakis(imidazole)dicopper(II), [Cu₂(C₇H₄NO₃S)₄(C₃H₄N₂)₄], $M_r = 1128.10$, monoclinic, $P2_1/n$, $a = 11.084(1)$, $b = 11.481(1)$, $c = 17.078(1)$ Å, $\beta = 95.391(7)^\circ$, $V = 2163.7$ Å³, $Z = 2$, $D_x = 1.73$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12.91$ cm⁻¹, $F(000) = 1148$, $T = 294$ K, final $R = 0.049$ for 3275 unique observations. The molecule is composed of two trigonal-bipyramidally coordinated Cu atoms with four saccharin groups and four imidazole groups. However, the four C₆H₄COSO₂N groups are not structurally identical, two of them are each coordinated to only one Cu atom through the N atom, while the other two saccharin groups act as bidentate bridging ligands for the two Cu atoms, forming a Cu^{II} dimer containing an eight-membered ring.

Introduction. Research on crystal structures of metal-saccharin complexes has been active in the last ten years (Kamenar & Jovanovski, 1982; Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983; Li, Lin, Liu & Huang, 1990). However, the results reported so far have been limited to mononuclear complexes. This paper reports a saccharin complex containing two trigonal-bipyramidally coordinated Cu atoms, forming an eight-membered dimer.

Experimental. Blue prismatic crystals were grown from aqueous solution. Cell dimensions and crystal orientation matrix determined on an AFC5R diffractometer by a least-squares treatment of the setting angles of 20 reflections in the range $10 < \theta < 15^\circ$. Crystal dimensions $0.12 \times 0.42 \times 0.48$ mm; intensities of reflections with indices h 0 to 14, k 0 to 14, l -22 to 22 with $2\theta < 55^\circ$ measured; ω - 2θ scans; ω scan width $(1.260 + 0.400 \tan \theta)^\circ$, graphite-monochromatized Mo $K\alpha$ radiation. Intensities of three

reflections measured every 2 h showed no evidence of crystal decay. 5508 reflections measured, 5245 unique. 3275 with $I > 3\sigma(I)$ were used in structure solution and refinement; $R_{\text{int}} = 0.024$. Data corrected for Lorentz factor, polarization factor and absorption effects (max. and min. transmission factors 1.194 and 0.885). Gaussian integration grid $6 \times 6 \times 6$. Space group $P2_1/n$ uniquely determined from systematic absences.

The crystal structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and later with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final round of calculations the H atoms were positioned on geometrical grounds (C—H 0.95 Å) and included (as riding atoms) in the structure-factor calculations. The final cycle of refinement included 316 variable parameters, $R = 0.049$, $wR = 0.064$, goodness-of-fit = 1.62, $w = 1/\sigma^2(F_o)$. Max. shift/e.s.d. = 0.04, electron density in final difference map ± 0.93 e Å⁻³; no chemically significant features. Scattering factors and anomalous-dispersion corrections of non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), and for H atoms from Stewart, Davidson & Simpson (1965). All calculations were made on a MicroVAX II computer using *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic coordinates, and details of molecular geometry are given in Tables 1† and 2. Fig. 1 is a view of the molecule prepared using *TEXSAN*.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, mean plane data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52964 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	B _{eq} (Å ²)
Cu	0.14121 (5)	0.15550 (5)	0.04019 (3)	2.00 (2)
S(1)	0.3227 (1)	0.3476 (1)	0.12295 (8)	3.10 (5)
S(2)	0.0211 (1)	-0.2345 (1)	-0.17704 (8)	2.83 (5)
O(1)	0.3817 (4)	0.2005 (5)	-0.0581 (3)	5.5 (2)
O(2)	0.2451 (4)	0.4461 (4)	0.1231 (3)	5.0 (2)
O(3)	0.3267 (4)	0.2807 (4)	0.1943 (2)	4.8 (2)
O(4)	0.1161 (3)	0.0131 (3)	-0.0518 (2)	2.8 (1)
O(5)	0.0170 (4)	-0.3510 (3)	-0.1463 (3)	4.7 (2)
O(6)	-0.0638 (3)	-0.2104 (4)	-0.2446 (2)	4.3 (2)
N(1)	0.2892 (3)	0.2661 (3)	0.0457 (2)	2.2 (2)
N(2)	0.0067 (3)	-0.1388 (3)	-0.1089 (2)	2.1 (2)
N(3)	0.0453 (3)	0.2559 (3)	-0.0346 (2)	2.2 (2)
N(4)	-0.0298 (4)	0.4087 (3)	-0.0968 (3)	3.0 (2)
N(5)	0.2370 (3)	0.0403 (3)	0.1024 (2)	2.2 (2)
N(6)	0.3114 (4)	-0.0756 (4)	0.1958 (2)	3.3 (2)
C(1)	0.6046 (5)	0.3380 (5)	0.0071 (4)	4.2 (3)
C(2)	0.6894 (5)	0.4046 (6)	0.0477 (5)	4.9 (3)
C(3)	0.6644 (5)	0.4630 (6)	0.1135 (4)	4.7 (3)
C(4)	0.5513 (6)	0.4567 (6)	0.1432 (3)	4.2 (3)
C(5)	0.4661 (4)	0.3846 (4)	0.1008 (3)	2.6 (2)
C(6)	0.4921 (4)	0.3274 (4)	0.0344 (3)	2.4 (2)
C(7)	0.3889 (4)	0.2517 (4)	-0.0032 (3)	1.8 (2)
C(8)	0.3171 (4)	-0.0547 (4)	-0.1530 (3)	2.8 (2)
C(9)	0.3909 (5)	-0.1053 (5)	-0.2042 (3)	3.5 (2)
C(10)	0.3534 (5)	-0.1978 (5)	-0.2509 (4)	3.8 (3)
C(11)	0.2407 (5)	-0.2446 (5)	-0.2491 (3)	3.5 (2)
C(12)	0.1681 (4)	-0.1959 (4)	-0.1962 (3)	2.4 (2)
C(13)	0.2031 (4)	-0.1028 (4)	-0.1499 (3)	1.9 (2)
C(14)	0.1054 (4)	-0.0668 (4)	-0.0993 (3)	1.9 (2)
C(15)	0.0600 (5)	0.3673 (4)	-0.0478 (3)	2.7 (2)
C(16)	-0.1070 (5)	0.3197 (5)	-0.1166 (3)	3.1 (2)
C(17)	-0.0603 (5)	0.2266 (4)	-0.0780 (3)	3.2 (2)
C(18)	0.2292 (5)	0.0058 (5)	0.1748 (3)	2.9 (2)
C(19)	0.3777 (5)	-0.0938 (5)	0.1338 (3)	3.1 (2)
C(20)	0.3309 (5)	-0.0223 (5)	0.0767 (3)	3.0 (2)

Table 2. Bond lengths (Å) and angles (°)

Cu—N(1)	2.069 (4)	Cu—O(4)	2.266 (3)	Cu—N(2')	2.113 (4)
Cu—N(3)	1.958 (4)	Cu—N(5)	1.948 (4)	S(1)—O(2)	1.420 (4)
S(1)—O(3)	1.438 (4)	S(1)—N(1)	1.631 (4)	S(1)—C(5)	1.722 (5)
S(2)—O(5)	1.439 (4)	S(2)—O(6)	1.445 (4)	S(2)—N(2)	1.619 (4)
S(2)—C(12)	1.749 (5)	O(1)—C(7)	1.103 (6)	O(4)—C(14)	1.223 (5)
N(1)—C(7)	1.457 (6)	N(2)—C(14)	1.369 (5)	C(1)—C(2)	1.351 (9)
C(1)—C(6)	1.378 (7)	C(3)—C(3)	1.36 (1)	C(3)—C(4)	1.398 (9)
C(4)—C(5)	1.404 (7)	C(5)—C(6)	1.364 (7)	C(6)—C(7)	1.529 (6)
C(8)—C(9)	1.381 (7)	C(8)—C(13)	1.384 (6)	C(9)—C(10)	1.369 (8)
C(10)—C(11)	1.363 (8)	C(11)—C(12)	1.383 (7)	C(12)—C(13)	1.365 (6)
C(13)—C(14)	1.505 (6)	N(3)—C(15)	1.312 (6)	N(3)—C(17)	1.367 (6)
N(4)—C(15)	1.327 (6)	N(4)—C(16)	1.355 (7)	C(16)—C(17)	1.334 (7)
N(5)—C(18)	1.308 (6)	N(5)—C(20)	1.371 (6)	N(6)—C(18)	1.331 (6)
N(6)—C(19)	1.360 (7)	C(19)—C(20)	1.342 (7)		
N(1)—Cu—O(4)	121.3 (1)	N(1)—Cu—N(2')	133.1 (1)		
O(4)—Cu—N(2')	105.6 (1)	N(3)—Cu—N(5)	171.9 (2)		
N(3)—Cu—N(1)	92.7 (2)	N(5)—Cu—O(4)	85.0 (1)		
Cu—O(4)—C(14)	177.3 (3)	O(4)—C(14)—N(2)	124.0 (4)		
C(14)—N(2)—Cu	129.9 (3)	C(2)—C(1)—C(6)	119.0 (6)		
C(1)—C(2)—C(3)	121.2 (6)	C(2)—C(3)—C(4)	122.3 (5)		
C(3)—C(4)—C(5)	115.2 (5)	C(4)—C(5)—C(6)	121.9 (5)		
C(4)—C(5)—S(1)	128.5 (4)	C(5)—C(6)—C(1)	120.4 (5)		
C(5)—C(6)—C(7)	114.5 (4)	C(6)—C(7)—N(1)	105.8 (4)		
C(6)—C(7)—O(1)	130.7 (5)	O(1)—C(7)—N(1)	123.4 (4)		
Cu—N(1)—S(1)	120.5 (2)	Cu—N(1)—C(7)	123.0 (3)		
S(1)—N(1)—C(7)	113.7 (3)	N(1)—S(1)—C(5)	96.2 (2)		
N(1)—S(1)—O(3)	111.4 (2)	O(2)—S(1)—O(3)	113.3 (3)		
O(2)—S(1)—N(1)	111.5 (2)	C(8)—C(13)—C(12)	120.1 (4)		
C(8)—C(13)—C(14)	128.4 (4)	C(12)—C(13)—C(14)	111.6 (4)		
O(4)—C(14)—C(13)	123.8 (4)	N(2)—C(14)—C(13)	112.0 (4)		
S(2)—N(2)—C(14)	111.4 (3)	S(2)—N(2)—Cu'	118.1 (2)		
O(5)—S(2)—O(6)	115.4 (3)	O(5)—S(2)—C(12)	111.4 (3)		
O(6)—S(2)—N(2)	110.1 (2)	N(2)—S(2)—C(12)	96.8 (2)		
Cu—N(3)—C(15)	128.1 (3)	Cu—N(3)—C(17)	126.4 (3)		
C(15)—N(3)—C(17)	105.1 (4)	N(3)—C(15)—N(4)	111.0 (4)		
C(15)—N(4)—C(16)	107.8 (4)	N(4)—C(16)—C(17)	105.9 (4)		
C(16)—C(17)—N(3)	110.1 (4)	Cu—N(5)—C(18)	129.8 (3)		
Cu—N(5)—C(20)	124.9 (3)	C(18)—N(5)—C(20)	105.3 (4)		

Discussion. The molecule of the title compound is composed of two Cu(C₆H₄COSO₂N)₂(C₃H₄N₂)₂ groups, which are related to each other by a crystallographic center of inversion as shown in Fig. 1. Atoms labeled with primes are related by the center of inversion to those listed in Table 1.

In this molecule each Cu atom has a trigonal-bipyramidal coordination with two N atoms and one O atom in the trigonal plane and two N atoms at the apexes. The Cu atom is located above the trigonal plane by 0.0170 (1) Å, this plane consisting of N(1), O(4) and N(2') from three saccharin ligands. The axial N atoms, N(3) and N(5) of two imidazole groups, are above and below the trigonal plane: N(3), 1.972 (3); N(5), -1.924 (3) Å. The equatorial bond lengths [Cu—N(1) 2.069 and Cu—N(2') 2.113 Å] are longer than those of axial bonds [Cu—N(3) 1.958 and Cu—N(5) 1.948 Å]. This is in good agreement with reported results (Raymond, Meek & Ibers, 1968).

There are four saccharin ligands in a molecule. While two of them are bidentate bridging ligands, the other two are monodentate ligands, namely the molecules with N(1) and N(1') are each only coordinated to one Cu atom through N. However, the molecules with N(2) and N(2') are both coordinated to two Cu atoms (Cu and Cu') through the N and O atoms. As a result, a Cu^{II} dimer is formed with two Cu atoms and two bridging saccharin ligands, resulting in an eight-membered ring Cu—O(4)—C(14)—N(2)—Cu'—O(4')—C(14')—N(2'). The eight-membered ring (CuOCN)₂ is the central part of the molecule, which is essentially planar, the deviations of atoms in the ring from the ring plane being less than 0.039 Å.

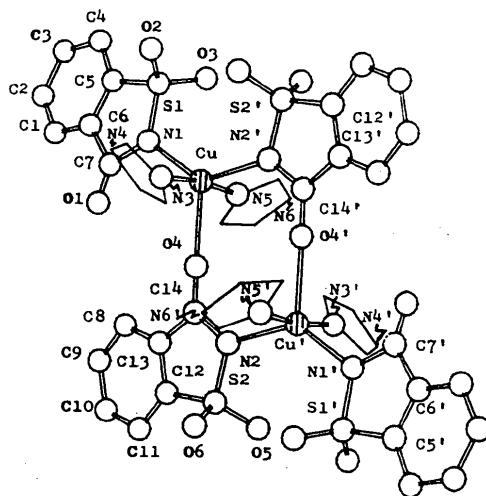


Fig. 1. Molecular configuration of the title compound.

Table 3. *Hydrogen bonds*

$Y \cdots H-X$ type	$Y \cdots H(\text{\AA})$	$Y \cdots X(\text{\AA})$	$Y \cdots H-X(^{\circ})$
O(2) \cdots H(10 ^m)—N(4 ^m)	2.409	2.911	112.8
O(3) \cdots H(14 ^m)—N(6 ^m)	2.359	3.021	126.4
O(5) \cdots H(10 ^m)—N(4 ^m)	2.050	2.947	156.8
O(6) \cdots H(15 ^m)—N(6 ^m)	2.380	2.953	118.6

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1/2-x, 1/2+y, 1/2-z$; (iii) $x, y-1, z$; (iv) $-1/2+x, -1/2-y, -1/2+z$. Primed atoms are related by the symmetry center.

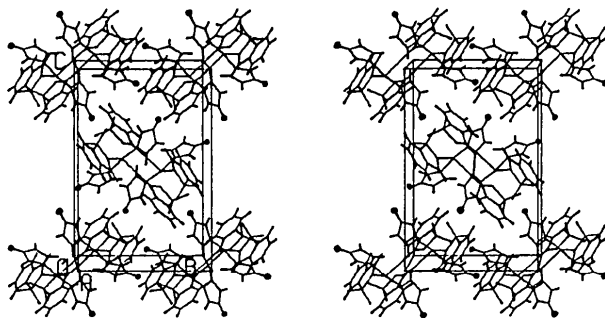


Fig. 2. Packing of the title compound in the unit cell along the a axis.

The two imidazole planes and the eight-membered-ring plane are nearly perpendicular to each other, the values of the dihedral angles being 86.7 (2), 85.8 (3) and 87.7 (2).

As can be seen in Table 3, there are two intermolecular three-center hydrogen bonds between the N—H from the imidazole group and the pair of sulfonyl O atoms of the saccharin ligand. The H atoms involved in these interactions are marked with filled circles in Fig. 2.

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Structure of a Five-Coordinated Nickel Complex: $[\text{Ni}\{(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2\}_2\text{P}(\text{C}_6\text{H}_5)_3]$

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Abstract. Bis(*O,O'*-diethyl dithiophosphato)(triphenylphosphine)nickel(II), $[\text{Ni}(\text{C}_4\text{H}_{10}\text{O}_2\text{PS}_2)_2\text{P}(\text{C}_6\text{H}_5)_3]$, $M_r = 691.45$, triclinic, $P\bar{1}$, $a = 12.985$ (2), $b = 13.748$ (2), $c = 9.389$ (1) \AA , $\alpha = 99.58$ (1), $\beta = 99.10$ (1), $\gamma = 84.12$ (1) $^\circ$, $V = 1627.0$ \AA^3 , $Z = 2$, $D_x = 1.41$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ \AA , $\mu = 10.18$ cm^{-1} , $F(000) = 720$, $T = 295$ K, final $R = 0.062$ for 5040 unique observations. The Ni atom in this molecule is coordinated by four

S atoms and one P atom, forming a square pyramid. The triphenylphosphine moiety is planar.

Introduction. $[\text{Ni}\{(\text{RO})_2\text{PS}_2\}_2]$ complexes have attracted broad attention in the study of high fungicidal and bacteriological activity (Livingstone & Mihkelson, 1970). Recently we have studied some reactions of $[\text{Ni}\{(\text{RO})_2\text{PS}_2\}_2]$ and the crystal structures of some adducts (You, Xu, Yu, Liu & Lin, 1986; Liu, Lin, Xu, Yu & You, 1987; Lin, Liu, Xu, Lin & You, 1987; Liu, Lin, Xu, Lin, Yu & You,

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