

0.088 $\{w = 4(F_o)^2 / [\sigma(F_o)^2]^2\}$ and quality of fit indicator $S = 2.967$. All shifts of 146 refined parameters were found to be smaller than 0.001σ . The highest peaks remaining on the resulting electron density map, measuring from 0.825 to 0.500 e Å⁻³, were in the immediate vicinity of the Cu and Br atoms. Atomic scattering factors were taken from Cromer & Waber (1974). All calculations were performed utilizing a PDP-11/60 minicomputer and Enraf-Nonius (1983) *SDP-Plus* software.

Final positional parameters and equivalent isotropic displacement parameters are listed in Table 1. Bond distances and angles between atoms are listed in Table 2.* An *ORTEPII* (Johnson, 1976) drawing and the atomic labeling scheme are shown in Fig. 1. A packing diagram is presented in Fig. 2.

* Lists of structure factors, complete bond distances and angles, anisotropic displacement parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55497 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1000]

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Structure of Bis(benzenesulfonato-*O*)tetrakis(pyridine-*N*)copper(II)

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Abstract. [Cu(C₆H₅O₃S)₂(C₅H₅N)₄], $M_r = 694.29$, monoclinic, $C2/c$, $a = 15.180$ (6), $b = 14.431$ (5), $c = 15.269$ (6) Å, $\beta = 96.38$ (4)°, $V = 3324$ (2) Å³, $Z = 4$, $D_x = 1.388$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 8.54$ cm⁻¹, $F(000) = 1436$, $T = 295$ K, $R = 0.067$, $wR = 0.087$ for 1141 independent reflections with $I \geq 3\sigma(I)$ and 207 variables. The [Cu(O₃-SC₆H₅)₂(C₅H₅N)₄] complex has a distorted *trans* octahedral stereochemistry. The bond angles about the Cu atom are consistent with this structure type. The important bond distances and angles are: Cu—O1 2.471 (8), S—Cl 1.785 (10) Å, Cu—O1—S 154.1 (6), O1—S—O2 112.3 (5), O1—S—O3 111.5 (5)°.

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Experimental. The title compound was prepared by reaction of metallic copper powder with diphenyl disulfide in pyridine solution. Slow diffusion of hexanes into the reaction solution afforded regular prismatic blue crystals at room temperature. A suitable single crystal for X-ray crystallography (0.26 × 0.34 × 0.31 mm) was mounted inside a glass capillary using fast drying epoxy glue. The unit-cell parameters were determined from 25 reflections with $12.78 < \theta < 24.16^\circ$. A total number of 2919 unique reflections with $2 < \theta < 25^\circ$ ($0 \leq h \leq 19$, $0 \leq k \leq 19$, $-19 \leq l \leq 19$) were collected (ω - 2θ scans) using an Enraf-Nonius X-ray automated diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Three standard reflections, monitored every 60 min, showed 3.3% variation in intensity; decay correction

Related literature. X-ray structures of the following two adducts were recently determined: copper(I) bromide with 2-bromopyridine and copper(I) chloride with 2-benzylpyridine (Healy, Kildea, Skelton, Waters & White, 1991).

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Table 1. *Positional parameters and equivalent isotropic displacement parameters* (\AA^2)
$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Cu	0.500	0.2706 (1)	0.750	3.52 (4)
S	0.2518 (2)	0.3020 (2)	0.7643 (2)	3.94 (6)
O1	0.3429 (5)	0.2709 (5)	0.7785 (5)	5.0 (2)
O2	0.2349 (5)	0.3600 (4)	0.6864 (4)	4.9 (2)
O3	0.1913 (6)	0.2266 (5)	0.7668 (6)	7.9 (2)
N1	0.500	0.4106 (6)	0.750	2.7 (2)
N2	0.4680 (6)	0.2701 (5)	0.6180 (5)	3.4 (2)
N3	0.500	0.1316 (6)	0.750	2.8 (2)
C1	0.2396 (7)	0.3728 (7)	0.8581 (6)	4.1 (3)
C1A	0.2633 (9)	0.4627 (8)	0.8574 (8)	7.0 (3)
C1B	0.4406 (8)	0.0841 (6)	0.7888 (7)	4.4 (3)
C1D	0.4281 (7)	0.4577 (6)	0.7073 (7)	4.2 (2)
C1C	0.5163 (8)	0.3181 (8)	0.5666 (7)	5.3 (3)
C2D	0.4285 (8)	0.5534 (6)	0.7128 (7)	4.9 (3)
C2A	0.260 (1)	0.5136 (9)	0.936 (1)	8.7 (5)
C2B	0.443 (1)	-0.0117 (7)	0.7952 (9)	6.7 (3)
C2C	0.493 (1)	0.318 (1)	0.4764 (8)	8.3 (4)
C3D	0.500	0.6016 (8)	0.750	4.7 (4)
C3C	0.4253 (9)	0.268 (1)	0.4383 (7)	6.8 (4)
C3B	0.500	-0.0582 (9)	0.750	6.2 (5)
C3A	0.226 (1)	0.475 (1)	1.001 (1)	12.0 (6)
C4C	0.3743 (8)	0.2242 (8)	0.4905 (7)	4.8 (3)
C4A	0.199 (2)	0.389 (1)	0.998 (1)	18.5 (7)
C5C	0.3976 (7)	0.2263 (7)	0.5799 (6)	4.0 (2)
C5A	0.205 (1)	0.3358 (9)	0.9250 (8)	11.3 (5)

Table 2. *Bond distances* (\AA) *and angles* ($^\circ$)

Cu—O1	2.471 (8)	C1—C5A	1.31 (2)
Cu—N1	2.020 (9)	C1A—C2A	1.41 (2)
Cu—N2	2.020 (7)	C1B—C2B	1.387 (14)
Cu—N3	2.006 (9)	C1D—C2D	1.384 (13)
S—O1	1.448 (8)	C1C—C2C	1.38 (2)
S—O2	1.455 (7)	C2D—C3D	1.359 (12)
S—O3	1.427 (9)	C2A—C3A	1.30 (3)
S—C1	1.785 (10)	C2B—C3B	1.35 (2)
N1—C1D	1.386 (11)	C2C—C3C	1.34 (2)
N2—C1C	1.327 (14)	C3C—C4C	1.34 (2)
N2—C5C	1.320 (13)	C3A—C4A	1.30 (3)
N3—C1B	1.324 (12)	C4C—C5C	1.371 (14)
C1—C1A	1.346 (15)	C4A—C5A	1.37 (2)
O1—Cu—O1	180.0 (8)	Cu—N3—C1B	121.1 (5)
O1—Cu—N1	89.9 (2)	C1B—N3—C1B	117.7 (9)
O1—Cu—N2	92.6 (3)	S—C1—C1A	119.6 (9)
O1—Cu—N3	87.4 (3)	S—C1—C5A	118.5 (9)
O1—Cu—N3	90.1 (2)	C1A—C1—C5A	122.0 (1)
N1—Cu—N2	90.2 (2)	C1—C1A—C2A	118.0 (1)
N1—Cu—N3	180.00 (0)	N3—C1B—C2B	122.0 (1)
N2—Cu—N2	179.6 (3)	N1—C1D—C2D	117.5 (9)
N2—Cu—N3	89.8 (2)	N2—C1C—C2C	120.0 (1)
O1—S—O2	112.3 (5)	C1D—C2D—C3D	122.0 (1)
O1—S—O3	111.5 (5)	C1A—C2A—C3A	119.0 (1)
O1—S—C1	103.9 (5)	C1B—C2B—C3B	118.0 (1)
O2—S—O3	113.9 (5)	C1C—C2C—C3C	122.0 (1)
O2—S—C1	107.6 (4)	C2D—C3D—C2D	118.0 (1)
O3—S—C1	106.9 (5)	C2C—C3C—C4C	118.0 (1)
Cu—O1—S	154.1 (6)	C2B—C3B—C2B	120.0 (1)
Cu—N1—C1D	119.3 (5)	C2A—C3A—C4A	122.0 (2)
C1D—N1—C1D	121.3 (9)	C3C—C4C—C5C	119.0 (1)
Cu—N2—C1C	120.0 (7)	C3A—C4A—C5A	121.0 (2)
Cu—N2—C5C	122.3 (7)	N2—C5C—C4C	124.0 (1)
C1C—N2—C5C	117.6 (8)	C1—C5A—C4A	118.0 (1)

applied. Experimental absorption corrections ranging from 1.00 to 0.98 (North, Phillips & Mathews, 1968) and a secondary-extinction correction of the form $F_c = F_o / (1 + gF_c)$, with $g = 1.511 \times 10^{-10}$, were applied. F_o were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from Cromer & Waber (1974). The structure was solved by the heavy-atom method for the positions of Cu and S atoms. All calculations were performed on a PDP-11 minicomputer utilizing

Enraf-Nonius (1983) *SDP-Plus* software. Positions of remaining non-H atoms were determined by least-squares refinements (on F) and difference electron density map analysis. Some H atoms were also found by this procedure; the remaining H-atom positions were calculated assuming standard geometry. The non-H atoms were refined anisotropically; H atoms were not refined. The asymmetric unit contains one half of the structural unit. The atoms N1, N3, C3D, C3B and the Cu atom reside on a twofold rotation axis in the cell which generates the full structure. The structure was refined to convergence giving $R = 0.067$ and $wR = 0.087$ $\{w = 4(F_o)^2 / [\sigma(F_o)^2]\}^2$ with quality of fit indicator $S = 1.893$. All shifts were smaller than 0.001σ . The three largest peaks still evident on the difference electron density map were located in the vicinity of the Cu and S atoms and were less than $0.414 e \text{\AA}^{-3}$. The most negative peak was $-0.457 e \text{\AA}^{-3}$. Final positional parameters and equivalent isotropic displacement parameters are supplied in Table 1. Important bond distances and angles are given in Table 2.* Fig. 1 shows an *ORTEP* representation (Johnson, 1976) of the whole molecule and also depicts the atomic labeling scheme.

Related literature. X-ray structures of the following copper(II) complexes were recently determined: $[\text{Cu}(\text{OSO}_2\text{OC}_{12}\text{H}_{25})_2(\text{N}_2\text{C}_2\text{H}_8)_2]$ (Birker, Crisp & Moore, 1977), $[\text{Cu}(\text{O}_3\text{SCF}_3)_2(\text{C}_9\text{H}_7\text{N})_4]$ (Al Sarraj, Gouteron, Jeannin & Jeannin, 1987), $[\text{Cu}(\text{O}_3\text{-SCF}_3)_2(\text{C}_5\text{H}_5\text{N})_4]$ (Haynes, Rettig, Sams, Trotter &

* Lists of structure factors, complete bond distances and angles, and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55496 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1001]

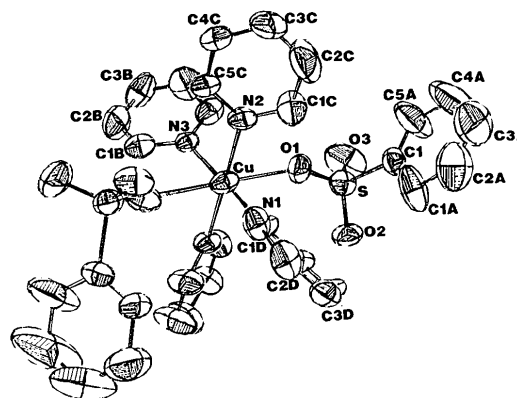


Fig. 1. *ORTEP* representation (Johnson, 1976) of the *trans*- $[\text{Cu}(\text{O}_3\text{SC}_6\text{H}_5)_2(\text{C}_5\text{H}_5\text{N})_4]$ complex. The ellipsoids are drawn at the 50% probability level.

Thompson, 1988) and [Cu(O₄S)(C₅H₅N)₄].H₂O (Kožíšek, Hricov & Langfelderová, 1989).

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Structure of an Allotropic Form of [Bis(trimethylsilyl)amido]dichloro-(η^5 -cyclopentadienyl)titanium

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Abstract. [TiCl₂(C₆H₁₈NSi₂)(C₅H₅)], $M_r = 344.3$, triclinic, $P\bar{1}$, $a = 8.831(4)$, $b = 14.270(8)$, $c = 6.774(8)$ Å, $\alpha = 91.98(8)$, $\beta = 99.33(9)$, $\gamma = 85.13(5)^\circ$, $V = 839.2(8)$ Å³, $Z = 2$, $D_x = 1.36$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.95$ mm⁻¹, $F(000) = 360$, $T = 185$ K. Full-matrix least-squares refinement based on 1583 reflections led to $R(F_o)$ and $wR(F_w)$ values of 0.042 and 0.053, respectively. The room-temperature unit cell is also triclinic with consistent parameters. This triclinic form is an allotropic modification of the monoclinic [CpTiCl₂{N(SiMe₃)₂}] [Bai, Roesky & Noltemeyer (1991). *Z. Anorg. Allg. Chem.* **595**, 21–26]. No significant difference is observed in the molecular structure of both forms, characterized by a tetrahedral environment of the Ti atom and a noticeably short [1.881(6) Å] Ti—N bond.

Experimental. [CpTiCl₂{N(SiMe₃)₂}] from LiN-(SiMe₃)₂ and CpTiCl₃ in toluene under nitrogen, recrystallized from toluene solution at 255 K. A moisture-sensitive orange crystal of dimensions 0.40 × 0.20 × 0.05 mm was protected by a film of mineral oil, stuck with Apiezon grease and quickly transferred to the nitrogen gas flow of a cooling device. Intensity data were recorded at 185 K on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions

were determined from setting angles of 25 reflections having $3.5 < \theta < 14.1^\circ$. 2277 reflections were measured using $\omega/2\theta$ scans with 2θ from 3 to 44° ($-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $0 \leq l \leq 7$) and scan width $(0.90 + 0.35 \tan \theta)^\circ$, with variable scan speed 0.97 – 8.24° min⁻¹. Intensities of three reflections ($\bar{1}01$, 141 , $0\bar{1}\bar{1}$) measured every 2 h showed 3.4% decay, for which correction was made. Corrections were applied for Lp effects, as well as for absorption by ψ scans (North, Phillips & Mathews, 1968); minimum and maximum relative transmission 0.83 and 0.99, respectively. 1925 reflections were unique; $R_{\text{int}} = 0.019$ for averaging redundant $\pm h \pm k 0$ reflections. Direct methods followed by Fourier and least-squares techniques using 1583 reflections having $F_o^2 > 3\sigma(F_o^2)$ based on counting statistics, were used to solve the structure. Full-matrix least-squares refinement was based on F_o , minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters for non-H atoms. All H atoms were located by ΔF map and included with constrained geometry (C—H = 0.97 Å) and with isotropic U_H kept fixed to 0.05 Å². Final $R = 0.042$, $wR = 0.053$, $S = 1.45$, for 154 variables, and with unit weights.† Maximum parameter

† Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55570 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1006]

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