Table 2. *Comparison of corresponding bond distances* (Å) *and angles* (°) *in* [Ni($C_{14}H_6N_8$)], [Ni(disn)$_2$], [Ni($C_{18}H_{14}N_4$)] *and free damn*

	[Ni($C_{14}H_6N_8$)]	[Ni(disn)$_2$]	[Ni($C_{18}H_{14}N_4$)]	damn
Ni–N(2)	1·851 (1)	1·827 (3)	1·870 (2)	
C(2)–C(2′)	1·360 (3)	1·403 (5)	1·399 (3)	1·363 (6)
C(2)–N(2)	1·397 (2)	1·331 (4)	1·418 (3)	1·392 (8)
N(2)–C(3)	1·343 (2)		1·327 (3)	
C(3)–C(4)	1·375 (2)		1·384 (4)	
C(1)–C(2)	1·425 (2)	1·438 (5)		1·439 (7)
N(1)–C(1)	1·132 (2)	1·135 (5)		1·165 (10)
N(2)–Ni–N(3)	94·1 (1)	95·7 (1)	94·8 (1)	
N(2)–C(2)–C(1)	122·6 (1)	124·4 (3)	126·6 (2)	117·6 (3)
N(2)–C(2)–C(2′)	114·6 (1)	113·2 (3)	113·6 (2)	124·1 (4)
C(1)–C(2)–C(2′)	122·8 (1)	122·4 (3)	119·9 (2)	118·1 (8)
C(2)–N(2)–C(3)	120·6 (1)		120·2 (2)	
Ni–N(2)–C(3)	126·9 (1)		125·9 (2)	
Ni–N(2)–C(2)	112·5 (1)	114·6 (2)	113·9 (2)	
C(4)–C(3)–N(2)	124·1 (2)		124·7 (2)	
C(3)–C(4)–C(3′)	123·9 (2)		124·1 (2)	
C(2)–C(1)–N(1)	178·2 (2)	177·8 (4)		179·8 (9)
Reference	This work	Peng *et al.* (1984)	Weiss *et al.* (1977)	Penfold & Lipscomb (1961)

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Structure of Triaqua(D,L-β,β-dimethylcysteato)copper(II) Dihydrate, [$Cu(C_5H_9NO_5S)(H_2O)_3$].$2H_2O$

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Abstract. $M_r = 348{\cdot}81$, monoclinic Cc, $a = 13{\cdot}605$ (2), $b = 11{\cdot}163$ (1), $c = 9{\cdot}560$ (2) Å, $\beta = 117{\cdot}07$ (2)°, $U = 1292{\cdot}9$ (7) Å^3, $Z = 4$, $D_m = 1{\cdot}785$ (5), $D_x = 1{\cdot}792$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) $= 1{\cdot}89$ mm^{-1}, $F(000) = 724$, $T = 297$ (1) K, $R_F = 0{\cdot}023$ for 1164 reflections. The structure contains Cu$^{\rm II}$ ions linked by *syn-anti* carboxylate bridges to form zigzag $\lnot$(Cu—O—C—O$\rlap{)}$— chains parallel to **c**. Each Cu$^{\rm II}$ ion is tetragonally coordinated. Equatorial NO_3 ligation is provided by the two carboxylate O atoms [1·949 (3) and 1·957 (3) Å] and the amino N atom [1·986 (3) Å] of the tridentate β,β-dimethylcysteate ligand, and one water molecule [1·983 (3) Å]. Two additional water molecules form weak axial bonds with Cu [2·471 (3) and 2·572 (5) Å] and complete the NO_5 coordination.

Introduction. We have been interested in copper complexes of penicillamine and related ligands because of their possible relevance to the chemotherapeutic treatment of Wilson's disease (Birker & Freeman, 1977) as well as their potential usefulness as electronic–structural models for the chromophores present in the blue copper proteins (Schugar, 1983). As part of these studies, a dimeric disulfide complex {bis[copper(II)–D-penicillamine disulfide].$9H_2O$ (Thich, Mastropaolo, Potenza & Schugar, 1974)} with an unusual copper–disulfide interaction, and a novel mixed-valence copper mercaptide cluster complex (Schugar, Ou, Thich, Potenza, Felthouse, Haddad, Hendrickson, Furey & Lalancette, 1980) have been prepared and characterized structurally. We report here the structure of the title compound, a copper(II) complex of the oxidized sulfonic acid derivative of D,L-penicillamine. Space-group and cell-dimension data for several related copper(II) complexes containing this ligand were reported by Crowfoot, Bunn, Rogers-Low & Turner-Jones (1949) in their classic X-ray investigation of the structure of penicillin.

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Experimental. The complex was prepared by adding 1·00 g of penicillaminic acid, obtained following a literature procedure (Abraham, Baker, Boon, Calam, Carrington, Chain, Florey, Freeman, Robinson & Sanders, 1949), to a slurry of excess $CuCO_3$ in 40 ml of H_2O. This mixture was boiled for 10 min and filtered; evaporation at room temperature yielded deep-blue crystals which were recrystallized from 50%(v/v) ethanol–water. Using the Faraday method, the magnetic moment at 298 K was found to be 2·02 (2) Bohr magnetons (1 Bohr magneton ≡ $9{\cdot}27 \times 10^{-24}$ JT^{-1}).

D_m by flotation in iodobenzene/CCl_4; blue prism $0{\cdot}15 \times 0{\cdot}22 \times 0{\cdot}48$ mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) consistent with $C2/c$ and Cc; Cc confirmed by successful solution of structure. Cell constants from setting angles of 25 reflections with $13{\cdot}36 \leq \theta \leq 22{\cdot}20°$; data corrected for Lorentz, polarization, and absorption (empirical) effects. Variation in intensity of 3 standard reflections <1%; 1189 unique reflections measured with $2 \leq 2\theta \leq 50°$; 1164 with $I \geq 2\sigma(I)$ used in refinement. Range of h,k,l; 0 to 16, 0 to 13, −11 to 11. Structure solved by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference Fourier map and at calculated positions; C—H distance 0·95 Å; H atoms not refined. Full-matrix least-squares refinement on F; all non-H atoms anisotropic; $w = 4F_o/[\sigma^2(F_o^2) + 0{\cdot}0016F_o^4]$; final $R_F = 0{\cdot}023$, $wR_F = 0{\cdot}030$, $S = 1{\cdot}23$, $\Delta_{max}/\sigma < 0{\cdot}01$, $\Delta\rho_{max}$ 0·55 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); programs from Enraf–Nonius (1983) *SDP*.

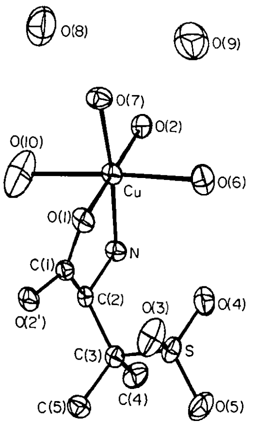

Fig. 1. View of the title complex showing the atom-numbering scheme. H atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Primed and unprimed atoms are related by the glide-plane operation.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cu	1·	0·92844 (3)	0·75	1·824 (7)
S	0·82013 (7)	1·26127 (9)	0·5756 (1)	2·31 (2)
O(1)	0·9706 (2)	0·9961 (2)	0·5467 (3)	2·12 (5)
O(2)	1·0323 (2)	0·8554 (2)	0·9524 (3)	2·23 (5)
O(3)	0·7932 (2)	1·2109 (3)	0·4232 (4)	3·87 (7)
O(4)	0·8024 (2)	1·1776 (3)	0·6797 (4)	3·47 (7)
O(5)	0·7630 (2)	1·3743 (3)	0·5641 (4)	3·46 (7)
O(6)	0·8000 (2)	0·9262 (3)	0·6707 (4)	3·25 (7)
O(7)	0·9887 (2)	0·7641 (2)	0·6654 (3)	2·64 (6)
O(8)	1·1744 (3)	0·6380 (4)	0·8403 (4)	5·6 (1)
O(9)	0·8063 (3)	0·6448 (4)	0·6423 (6)	6·4 (1)
O(10)	1·2034 (4)	0·9390 (5)	0·8060 (5)	6·4 (1)
N	1·0276 (2)	1·0981 (3)	0·8197 (3)	1·81 (6)
C(1)	1·0090 (3)	1·1003 (3)	0·5538 (4)	1·73 (7)
C(2)	1·0345 (3)	1·1767 (3)	0·7000 (4)	1·52 (6)
C(3)	0·9674 (3)	1·2939 (3)	0·6693 (4)	1·76 (7)
C(4)	0·9962 (3)	1·3572 (4)	0·8261 (4)	2·68 (8)
C(5)	0·9906 (3)	1·3801 (4)	0·5625 (4)	2·76 (8)

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

Numbers in parentheses are estimated standard deviations in the least-significant digits. Primed and unprimed atoms are related by the glide-plane operation.

Cu—Cu′	5·0397 (2)	S—O(5)	1·460 (3)
Cu—O(1)	1·949 (3)	S—C(3)	1·821 (3)
Cu—O(2)	1·957 (3)	O(1)—C(1)	1·265 (4)
Cu—O(6)	2·471 (3)	O(2′)—C(1)	1·250 (5)
Cu—O(7)	1·983 (3)	N—C(2)	1·479 (5)
Cu—O(10)	2·572 (5)	C(1)—C(2)	1·536 (5)
Cu—N	1·986 (3)	C(2)—C(3)	1·545 (5)
S—O(3)	1·445 (4)	C(3)—C(4)	1·539 (5)
S—O(4)	1·463 (4)	C(3)—C(5)	1·536 (6)

O(1)—Cu—O(2)	177·8 (1)	O(4)—S—O(5)	110·8 (2)
O(1)—Cu—O(6)	90·0 (1)	O(4)—S—C(3)	106·2 (2)
O(1)—Cu—O(7)	90·5 (1)	O(5)—S—C(3)	107·1 (2)
O(1)—Cu—O(10)	84·4 (1)	Cu—O(1)—C(1)	114·3 (2)
O(1)—Cu—N	83·5 (1)	Cu—N—C(2)	112·0 (2)
O(2)—Cu—O(6)	91·1 (1)	O(2′)—C(1)—C(2)	117·0 (3)
O(2)—Cu—O(7)	87·6 (1)	O(1)—C(1)—C(2)	118·4 (3)
O(2)—Cu—O(10)	94·4 (1)	O(1)—C(1)—O(2′)	124·5 (3)
O(2)—Cu—N	98·2 (1)	N—C(2)—C(1)	107·9 (3)
O(6)—Cu—O(7)	89·8 (1)	N—C(2)—C(3)	114·1 (3)
O(6)—Cu—O(10)	174·4 (1)	C(1)—C(2)—C(3)	115·3 (2)
O(6)—Cu—N	97·3 (1)	S—C(3)—C(2)	110·3 (2)
O(7)—Cu—O(10)	90·2 (1)	S—C(3)—C(4)	107·8 (3)
O(7)—Cu—N	170·8 (2)	S—C(3)—C(5)	108·1 (2)
O(10)—Cu—N	82·3 (2)	C(2)—C(3)—C(4)	109·7 (3)
O(3)—S—O(4)	113·1 (2)	C(2)—C(3)—C(5)	112·0 (3)
O(3)—S—O(5)	112·3 (2)	C(4)—C(3)—C(5)	108·8 (3)
O(3)—S—C(3)	106·9 (2)		

Table 3. *Possible hydrogen-bonding contacts*

D	H	A	D—H···A (°)	D···A (Å)	H···A (Å)	D—H (Å)
N	H1N	O(5^{i})	156·3 (3)	3·000 (4)	2·13	0·93
N	H2N	O(4)	131·5 (2)	2·870 (4)	2·11	1·00
O(6)	H2(O6)	O(4)	160·8 (2)	2·807 (5)	1·83	1·02
O(7)	H1(O7)	O(9)	152·6 (2)	2·735 (6)	1·97	0·84
O(7)	H2(O7)	O(8)	175·8 (3)	2·704 (5)	1·80	0·90
O(8)	H2(O8)	O(6^{ii})	165·8 (3)	2·915 (5)	1·96	0·97
O(10)	H1(O10)	O(5^{iii})	147·3 (3)	2·868 (7)	1·95	1·03

Symmetry code: (i) $\frac{1}{2} + x, \frac{5}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the title complex showing the atom-numbering scheme is given in Fig. 1, while important bond distances and angles are given in Table 2. The structure contains Cu^{II} ions linked by carboxylate bridges to form zigzag $\dashv$Cu—O—C—O$\vdash$ chains parallel to **c**. Each Cu^{II} ion is tetragonally coordinated. Equatorial ligation is provided by the two *trans* carboxylate O atoms, the amine N atom of the tridentate *β,β*-dimethylcysteate ligand, and one water molecule [O(7)]. Two additional water molecules [O(6), O(10)] form weak axial bonds with Cu and complete the NO_5 coordination. Equatorial bond distances and angles agree well (±*ca* 0·02 Å) with those reported for other rhombically distorted Cu complexes [Cu—O(carboxylate), Cu—NH_2 (Ou, Powers, Thich, Felthouse, Hendrickson, Potenza & Schugar, 1978); Cu—OH_2(equatorial) (Sheldrick, 1981; Walsh & Hathaway, 1980)]. In contrast, the Cu—OH_2(axial) distances [2·471 (3), 2·572 (5) Å] are substantially longer than that reported for a copper(II) complex of guanosine 2′-monophosphate [2·336 (10) Å (Sheldrick, 1981)] and significantly shorter than that in bis(*N*-acetyl-DL-tryptophanato)diaquabis(pyridine)-copper(II) [2·61 (1) Å (Battaglia, Corradi, Marcotrigiano, Menabue & Pellacani, 1980)]. In the tridentate ligand, the geometric features are similar to those reported for D-*β,β*-dimethylcysteic acid (Calvo, Faggiani, Harvey, Howard-Lock, Kean & Lock, 1984) except for the carboxylate group which is protonated in the free acid and deprotonated in the title complex. The bound axial and equatorial water molecules are involved in an elaborate hydrogen-bonding network with the lattice water molecules that serves to link the carboxylate-bridged chains together to form a three-dimensional network. Some details of the hydrogen-bonding network, which also includes hydrogen bonds involving the amine and sulfonic acid groups, are given in Table 3.

Successive Cu^{II} ions within the bridged carboxylate $\dashv$O—C—O—Cu$\vdash$ chain are related by the glide-plane operation and are in the *syn-anti* conformation, a conformation that has been observed previously in copper formate (Barclay & Kennard, 1961), copper citrate (Mastropaolo, Powers, Potenza & Schugar, 1976) and $[Cu_2(ClCH_2COO)_3(\text{ethylsalicylideneamine})(C_2H_5OH)]_\infty$ (Butcher, Overman & Sinn, 1980). Each $\dashv$O—Cu—O—C$\vdash$ [but not $\dashv$Cu—O—C—O$\vdash$ unit is planar to ±0·005 Å and the dihedral angle between adjacent $\dashv$O—Cu—O—C$\vdash$ groups is 46·2 (3)°. The shortest Cu···Cu′ distance in the structure [5·0397 (2) Å] occurs between successive Cu atoms in the chain; this distance is considerably shorter than that reported [5·476 (1) Å] for the acetate bridge in the salicylideneamine complex above. As expected for *syn-anti* bridges, the observed magnetic moment demonstrates that the carboxylate bridge in the title complex does not provide an effective pathway for magnetic exchange between Cu atoms.

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42137 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.