

selected bond distances and angles in Table 2.* Projections of the structure in both the *bc* and the *ac* planes are shown in Fig. 1.

Related literature. The crystal structure of Mn₃(CH₃COO)₆(H₂O)₄.2H₂O is closely related to that of the octahydrate Mn₃(CH₃COO)₆(H₂O)₄.8H₂O which was previously reported as Mn(CH₃COO)₂.4H₂O by Bertaut, Duc, Burllet, Burllet, Thomas & Moreau (1974). The layers comprise Mn₃(OAc)₆(H₂O)₄ units in both structures. In manganese acetate octahydrate, the two O atoms in all of the acetate groups

coordinate to two different Mn^{II} ions, whereas in the dihydrate only two thirds of the acetate groups are bridged in this way. The rest of the acetates coordinate to two Mn^{II} ions through only one O atom, O(1). In addition, the interlayer distance is larger (9.7 versus 8.2 Å) in Mn₃(CH₃COO)₆(H₂O)₄.8H₂O because there are twelve more water molecules per unit cell in the interlayer region than in the structure of the dihydrate.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54005 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,7-Bis(benzimidazol-2-yl)-2,6-dithiaheptanecopper(I) Perchlorate at 233 K

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Abstract. [Cu(C₁₉H₂₀N₄S₂)ClO₄], *M_r* = 531.52, monoclinic, *C2/c*, *a* = 14.166 (4), *b* = 17.571 (5), *c* = 9.942 (2) Å, β = 118.08 (2)°, *V* = 2183.3 Å³, *Z* = 4, *D_x* = 1.617 g cm⁻³, Cu *Kα*, λ = 1.54056 Å, μ = 46.1 cm⁻¹, *F*(000) = 1088, *T* = 233 K, the final *R* value is 0.053 for 1039 significant [*I* > 3σ(*I*)] reflections. The Cu^I ion is only linearly coordinated by two pyridine N atoms of the benzimidazole groups of the BBDHP ligand [Cu—N = 1.908 (4) Å]. The thioether S atoms do not have significant bonding contacts with the copper ion [Cu—S = 2.876 (2) Å]. The cation and perchlorate anion are linked by a hydrogen bond.

Experimental. A colourless single crystal of approximate dimensions 0.10 × 0.15 × 0.10 mm was sealed in a capillary. Because the crystals decompose at

room temperature all X-ray investigations were performed at 233 K. The systematic absences observed suggested the space group to be either *Cc* or *C2/c*. For calculations the centrosymmetric space group *C2/c* was chosen, and later confirmed by successful refinement of the structure. In the final full-matrix least-squares refinement all non-H atoms were assigned anisotropic temperature parameters; each atom of the perchlorate anion was allowed an individual isotropic temperature factor. The disordered perchlorate anion was assumed to occupy two alternative orientations related by a crystallographic two-fold axis, and their multiplicities were also refined, resulting in an occupancy of 0.5. The calculated H-atom positions were used only for structure factor calculations with *B*_{iso} fixed at 4 Å². More details of the intensity data collection, structure solution and refinement are listed in Table 1. Final atomic coordinates are given in Table 2, selected distances and

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Table 1. *Data-collection and structure-refinement parameters*

Crystal shape	Prism
Diffractometer	Enraf-Nonius CAD-4
Method of intensity measurement	ω/θ
Number and θ range (°) of reflections for lattice parameters	25, 8–36
Method used for absorption correction	<i>DIFABS</i> (Walker & Stuart, 1983)
Min., max. and ave. absorption correction	0.646, 1.415 and 1.010
Max. $(\sin^2\theta)/\lambda$ (\AA^{-1})	0.59
Range of h, k and l	0→16, 0→20 and -11→11
Standard reflections	314, 170
Interval (h)	1, no intensity variation
Total reflections measured, θ range (°)	1967, 6–65
Number of unobserved reflections	643, 71 systematic absences included
Number of unique reflections, R_{int}	1825, 0.045
Number of observed reflections	1039 where $I > 3\sigma(I)$
Method used to solve structure	Direct methods
Use of F or F^2 in LS refinement	F
Method of locating H atoms	Calculated in idealized positions with $d(C-H) = 0.95 \text{ \AA}$
Weighting scheme	$1/\sigma^2$
Parameters refined	145
R	0.053
wR	0.053
$(\Delta/\sigma)_{max}$	0.001
Max. height in final ΔF map ($e \text{ \AA}^{-3}$)	2.86
Error in an observation of unit weight	7.11 (1) $\times 10^{-7}$ (Zachariasen, 1963)
Secondary-extinction coefficient	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2A)
Sources of atomic scattering factors	<i>MicroVAX II</i> <i>SHELXS86</i> (Sheldrick, 1986) <i>VAX/SDP</i> (Frenz, 1978)
Computer used	
Programs used	

Table 2. *Positional and equivalent isotropic thermal parameters U_{eq} (\AA^2)*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	0.500	0.12652 (9)	0.250	0.0488 (7)
Ligand				
S	0.3937 (1)	0.0024 (1)	0.3117 (2)	0.0528 (8)
N(1)	0.3578 (4)	0.1395 (3)	0.0886 (5)	0.042 (2)
N(2)	0.1916 (4)	0.1041 (3)	-0.0716 (6)	0.046 (3)
C(1)	0.3227 (5)	0.1788 (4)	-0.0487 (7)	0.044 (3)
C(2)	0.3755 (6)	0.2339 (4)	-0.0902 (8)	0.061 (4)
C(3)	0.3196 (6)	0.2615 (4)	-0.2374 (8)	0.070 (4)
C(4)	0.2163 (6)	0.2365 (5)	-0.3382 (8)	0.068 (4)
C(5)	0.1649 (6)	0.1836 (5)	-0.2971 (8)	0.060 (4)
C(6)	0.2200 (5)	0.1559 (4)	-0.1490 (7)	0.046 (3)
C(7)	0.2751 (5)	0.0967 (4)	0.0694 (7)	0.042 (3)
C(8)	0.2684 (5)	0.0471 (4)	0.1866 (7)	0.055 (4)
C(9)	0.3970 (5)	-0.0656 (4)	0.1780 (8)	0.070 (4)
C(10)	0.500	-0.1103 (7)	0.250	0.098 (7)
Perchlorate*				
Cl(1)	0.4916 (3)	0.4464 (2)	0.6812 (4)	4.45 (7)
O(11)	0.3850 (7)	0.4305 (6)	0.634 (1)	6.9 (2)
O(21)	0.5199 (9)	0.4165 (8)	0.578 (1)	8.2 (3)
O(31)	0.5032 (8)	0.5298 (5)	0.684 (1)	5.7 (2)
O(41)	0.558 (1)	0.4184 (9)	0.810 (2)	8.8 (4)

* Atoms refined isotropically and with occupation factors of 0.5.

angles in Table 3.* A *SCHAKAL* (Keller, 1988) plot of the molecule is shown in Fig. 1, a stereoview of the unit cell in Fig. 2.

* Lists of structure factors, H-atom positions, bond distances and angles, torsion angles, least-squares planes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54029 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected distances (\AA) and angles ($^\circ$)*

Cu—N(1)	1.908 (4)	Cu—S	2.876 (2)	
S—C(8)	1.799 (7)	S—C(9)	1.805 (8)	
N(1)—C(1)	1.395 (9)	N(1)—C(7)	1.328 (9)	
N(2)—C(6)	1.37 (1)	N(2)—C(7)	1.349 (6)	
C(1)—C(2)	1.41 (1)	C(1)—C(6)	1.380 (8)	
C(2)—C(3)	1.383 (9)	C(3)—C(4)	1.399 (9)	
C(4)—C(5)	1.36 (1)	C(5)—C(6)	1.390 (9)	
C(7)—C(8)	1.49 (2)	C(9)—C(10)	1.509 (9)	
S—Cu—S				
S—Cu—S	81.38 (7)	S—Cu—N(1)	79.5 (2)	
S—Cu—N(1')	111.3 (2)	N(1)—Cu—N(1')	166.3 (2)	
C(8)—S—C(9)	98.0 (4)	C(1)—N(1)—C(7)	104.8 (4)	
C(6)—N(2)—C(7)	107.6 (6)	N(1)—C(1)—C(2)	129.6 (5)	
N(1)—C(1)—C(6)	109.5 (7)	C(2)—C(1)—C(6)	121.0 (6)	
C(1)—C(2)—C(3)	115.8 (6)	C(2)—C(3)—C(4)	122.5 (9)	
C(3)—C(4)—C(5)	121.9 (7)	C(4)—C(5)—C(6)	116.4 (6)	
N(2)—C(6)—C(1)	106.0 (6)	N(2)—C(6)—C(5)	131.3 (6)	
C(1)—C(6)—C(5)	122.7 (8)	N(1)—C(7)—N(2)	112.2 (6)	
N(1)—C(7)—C(8)	126.4 (5)	N(2)—C(7)—C(8)	121.4 (6)	
S—C(8)—C(7)	113.0 (5)	S—C(9)—C(10)	110.5 (4)	
C(9)—C(10)—C(9')	117.2 (8)	Anion		
Cl(1)—O(21) 1.37 (2)				
Cl(1)—O(31) 1.47 (1)				
Cl(1)—O(21) 1.37 (2)				
Cl(1)—O(41) 1.28 (1)				
Hydrogen bond				
O(11)—Cl(1)—O(21)	109.0 (7)	O(21)—Cl(1)—O(31)	109.2 (8)	
O(11)—Cl(1)—O(31)	107.5 (6)	O(21)—Cl(1)—O(41)	106 (1)	
O(11)—Cl(1)—O(41)	115.6 (9)	O(31)—Cl(1)—O(41)	109.9 (8)	
N(2)—H(20)—O(31) 140.8 (5)				
N(2)—H(20)—O(31')				178.3 (5)

Symmetry operator: (i) $-x, y, -0.5 - z$.

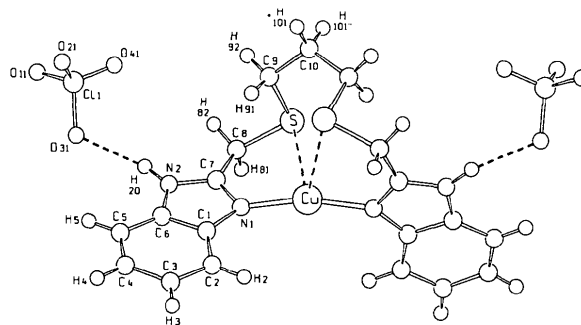
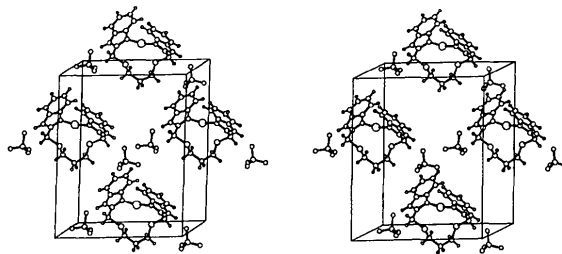


Fig. 1. View of the molecule with the atom-labelling scheme.

Fig. 2. Stereoview of the unit cell. **b** is vertical, **a** is horizontal and **c** is in the plane of the paper.

Related literature. The structure determination is part of our studies of transition-metal complexes derived from potentially quadridentate NSSN ligands (Castiñeiras, Hiller, Strähle, Paredes & Sordo, 1985; Castiñeiras, Carballo, Bermejo, Gayoso, Molleda, Hiller & Strähle, 1988; Castiñeiras, Carballo, Hiller, Montero, Pena & Strähle, 1990; Castiñeiras, Hiller, Strähle, Carballo, Bermejo & Gayoso, 1990; Castiñeiras, Carballo, Hiller & Strähle, 1990*a,b*, 1991; Hiller, Strähle, Castiñeiras, Carballo, Bermejo & Gayoso, 1990).

The structural parameters of [Cu(BBDHP)]ClO₄ can also be compared with those found in [Cu(BBDHP)](PF₆)_{0.66}(BF₄)_{0.34} (Schilstra, Birker, Verschoor & Reedijk, 1982).

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Structure of Dichloro(iodo)bis(triphenylphosphine oxide)thallium(III) at 223 K

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Abstract. [Tl(Cl)₂I]{P(C₆H₅)O₂}]₂, *M*_r = 958.77, monoclinic, *P*₂₁/*c*, *a* = 14.738 (1), *b* = 14.466 (6), *c* = 17.194 (1) Å, β = 107.98 (1)°, *V* = 3486.7 Å³, *Z* = 4, *D*_x = 1.826 g cm⁻³, *M*o *K*α, λ = 0.70930 Å, μ = 58.3 cm⁻¹, *F*(000) = 1840, *T* = 223 K, final *R* = 0.062 for 4967 significant [*I* > 3σ(*I*)] reflections. The structure consists of discrete TlCl₂I(tppo)₂ molecules (tppo = triphenylphosphine oxide) which have a distorted trigonal bipyramidal geometry. The Tl atom is coordinated to two Cl atoms and an I atom in equatorial positions, Tl—Cl = 2.412 (2) and 2.400 (5) Å, and Tl—I = 2.635 (2) Å, and by two

tppo ligands in axial positions, Tl—O = 2.38 (2) Å. The crystal structure is isotypic with those of TlBr₃(tppo)₂, TlBr₂I(tppo)₂, TlBrI₂(tppo)₂ and TlClBrI(tppo)₂.

Experimental. A yellow single crystal of approximate dimensions 0.30 × 0.20 × 0.15 mm was sealed in a glass fibre. Because the crystals decompose at room temperature all X-ray investigations were performed at 223 K. The structure was solved using direct methods which revealed the positions of all non-H atoms. In the final full-matrix least-squares refinement all non-H atoms were assigned anisotropic temperature parameters, and the calculated

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