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Acetato(3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane)silver(I) Dihydrate, [Ag(C₂₀H₄₂N₂S₂)(C₂H₃O₂)]·2H₂O

BY GEORGE FERGUSON, ROBERT MCCRINDLE AND MASOOD PARVEZ

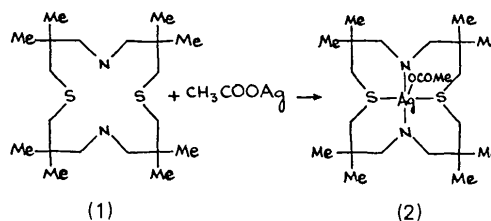
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Abstract. $M_r = 577.6$, triclinic, $P\bar{1}$, $a = 10.818(2)$, $b = 12.662(2)$, $c = 10.457(1)$ Å, $\alpha = 101.11(1)$, $\beta = 103.23(1)$, $\gamma = 89.77(2)^\circ$, $V = 1366.9$ Å³, $Z = 2$, $D_x = 1.40$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.8$ cm⁻¹, $F(000) = 612$, $T = 293$ K. Final $R = 0.026$ for 4164 observed reflections. The Ag atom has a square-pyramidal coordination distorted towards trigonal bipyramidal with axial N atoms [N–Ag–N 179.3(1)°] and equatorial acetato O and S atoms [S–Ag–O 98.0(1) and 101.4(1), S–Ag–S 160.6(1)°]. Principal dimensions are: Ag–S both 2.589(1), Ag–N 2.481(2) and 2.430(2), and Ag–O 2.686(2) Å; the macrocyclic ligand has the *t,t,t* configuration with all six-membered rings in twist-boat conformations.

Introduction. In recent publications we have reported the preparation of the macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (1) (McCrindle, McAlees & Stephenson, 1981) and the results of structural studies on the derived complexes [PdL](PF₆)₂ (where $L = 1$) (McCrindle, Ferguson, McAlees, Parvez & Stephenson, 1982) and [PdL]Cl₂·2H₂O (Ferguson, McCrindle, McAlees, Parvez & Stephenson, 1983). The present paper deals with the X-ray crystallographic study of the structure of the complex (2) produced (McCrindle, Ferguson, McAlees & Stephenson, 1983) by mixing a solution of (1) in acetonitrile with a suspension of silver(I) acetate in the same solvent, removing the acetonitrile by distillation *in vacuo*, and crystallization of the residue from acetone.

Experimental. Colourless crystals of (2)·2H₂O from acetone, 0.20 × 0.25 × 0.40 mm. CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflec-



tions with θ in range $10 < \theta < 15^\circ$ used to determine lattice constants; for data collection $2 < \theta < 25^\circ$ ($h - 12$ to $+12$, $k 0$ to -15 , $l - 12$ to $+12$), $\omega - 2\theta$ scans, ω -scan width $(0.60 + 0.35 \tan \theta)^\circ$; intensities of three reflections monitored every 3 h of exposure time showed no significant decay. Lp corrections, absorption correction not considered necessary; 4799 unique reflections, 4164 (86.8%) with $I > 3\sigma(I)$ where $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$, S = scan count and B = time-averaged background count. Structure solved by heavy-atom method using the *NRC Crystal Structure Package* (Larson & Gabe, 1978) and the PDP-8 computer associated with the CAD-4 diffractometer. Refinement by block-diagonal least-squares calculations on F with anisotropic thermal parameters. Coordinates for all but one of the H atoms determined from difference syntheses and included (with fixed isotropic thermal parameters) but not refined in subsequent calculations. Final $R = 0.026$, $R_w = 0.028$ for 4164 observed data, $R = 0.032$ for all data; $w = 1/\sigma^2(F)$. $\Delta\rho -0.3$ to 0.3 e Å⁻³. $(\Delta/\sigma)_{\max} = 0.06$ for U_{11} of C(13), $(\Delta/\sigma)_{\text{mean}} = 0.03$. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), allowance made for anomalous dispersion (Cromer & Liberman, 1970). Other computer programs used included *XANADU* (Roberts & Sheldrick, 1975) and *ORTEPII* (Johnson, 1976).

Discussion. Final fractional coordinates with equivalent isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions.*

The macrocyclic complex (Fig. 1) has the *t,t,t* configuration (Fig. 2) where all four six-membered rings (Ag,S,C,C,C,N) have twist-boat conformations and the N—H groups have *cis* configuration.

The Ag atom has a square-pyramidal coordination distorted towards trigonal bipyramidal with axial N atoms [N—Ag—N 179.3 (1)°] and equatorial acetato O and S atoms [S—Ag—S 160.6 (1), S—Ag—O 98.0 (1) and 101.4 (1)°]. Alternatively, the displacements of the atoms from the N₂S₂Ag plane are: N both 0.175 (1), S —0.261 (1) and —0.263 (1), and Ag 0.174 (1) Å. The Ag—S [both 2.589 (1) Å] and Ag—N [2.481 (2) and 2.430 (2) Å] distances are all within the ranges of distances found in other silver(I) macrocycle complexes, e.g. Ag—S 2.539–2.855 (2) and Ag—N 2.453–2.534 (7) Å in 1-oxa-4,13-dithia-7,10-diazacyclopentadecanesilver(I) thiocyanate (Louis & Weiss, 1977), Ag—S 2.526–3.005 (2) and Ag—N 2.448–2.559 (5) Å

* Lists of structure factors, anisotropic thermal parameters, torsion angles, hydrogen-bond distances, mean-plane data, H coordinates and dimensions involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38957 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates for (2) and B_{eq} (Å²) values with *e.s.d.*'s in parentheses

$$B_{eq} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Ag	0.39991 (2)	0.20850 (2)	0.09575 (2)	4.01 (1)
S(1)	0.40413 (6)	0.25228 (6)	−0.13509 (7)	2.80 (3)
S(2)	0.38098 (6)	0.10028 (6)	0.27721 (7)	2.83 (3)
N(1)	0.1665 (2)	0.2282 (2)	0.0479 (2)	2.6 (1)
N(2)	0.6285 (2)	0.1886 (2)	0.1451 (2)	2.5 (1)
C(1)	0.2863 (2)	0.3536 (2)	−0.1133 (3)	2.7 (1)
C(2)	0.1498 (2)	0.3055 (2)	−0.1626 (2)	2.7 (1)
C(3)	0.1257 (2)	0.2099 (2)	−0.0997 (2)	2.7 (1)
C(4)	0.0597 (3)	0.3958 (2)	−0.1308 (3)	3.7 (2)
C(5)	0.1206 (3)	0.2650 (3)	−0.3160 (3)	3.8 (2)
C(6)	0.1133 (2)	0.1416 (2)	0.0967 (3)	2.8 (1)
C(7)	0.1275 (2)	0.1605 (2)	0.2497 (3)	2.8 (1)
C(8)	0.2640 (2)	0.1933 (2)	0.3299 (3)	2.8 (1)
C(9)	0.0421 (3)	0.2507 (2)	0.2931 (3)	3.7 (2)
C(10)	0.0843 (3)	0.0554 (2)	0.2818 (3)	4.2 (2)
C(11)	0.5257 (2)	0.1710 (2)	0.3848 (2)	2.7 (1)
C(12)	0.6473 (2)	0.1166 (2)	0.3599 (3)	2.8 (1)
C(13)	0.6555 (2)	0.0962 (2)	0.2120 (3)	2.8 (1)
C(14)	0.6546 (3)	0.0065 (3)	0.4018 (3)	4.5 (2)
C(15)	0.7594 (3)	0.1906 (3)	0.4468 (3)	3.8 (2)
C(16)	0.6648 (2)	0.1671 (2)	0.0150 (2)	2.7 (1)
C(17)	0.6691 (2)	0.2659 (2)	−0.0495 (2)	2.6 (1)
C(18)	0.5503 (2)	0.3330 (2)	−0.0556 (2)	2.7 (1)
C(19)	0.7825 (3)	0.3421 (2)	0.0287 (3)	3.4 (1)
C(20)	0.6875 (3)	0.2243 (2)	−0.1928 (3)	3.7 (2)
C(21)	0.5547 (3)	0.4556 (2)	0.3081 (3)	3.3 (1)
C(22)	0.5515 (3)	0.5682 (2)	0.3895 (3)	4.3 (2)
O(1)	0.4512 (2)	0.4087 (2)	0.2426 (2)	4.1 (1)
O(2)	0.6607 (2)	0.4162 (2)	0.3101 (2)	4.4 (1)
O(3)	0.2082 (2)	0.4701 (2)	0.2233 (2)	6.0 (2)
O(4)	0.8708 (2)	0.4803 (2)	0.5178 (3)	7.8 (2)

Table 2. Molecular dimensions with *e.s.d.*'s in parentheses

(a) Bond distances (Å)			
Ag—S(1)	2.589 (1)	C(1)—C(2)	1.534 (4)
Ag—S(2)	2.589 (1)	C(2)—C(3)	1.534 (4)
Ag—N(1)	2.481 (2)	C(2)—C(4)	1.538 (4)
Ag—N(2)	2.430 (2)	C(2)—C(5)	1.545 (4)
Ag—O(1)	2.686 (2)	C(6)—C(7)	1.543 (4)
O(1)—C(21)	1.254 (3)	C(7)—C(8)	1.536 (4)
O(2)—C(21)	1.245 (4)	C(7)—C(9)	1.532 (4)
C(21)—C(22)	1.518 (4)	C(7)—C(10)	1.533 (4)
S(1)—C(1)	1.825 (3)	C(11)—C(12)	1.534 (4)
S(1)—C(18)	1.822 (3)	C(12)—C(13)	1.541 (4)
S(2)—C(8)	1.830 (3)	C(12)—C(14)	1.536 (4)
S(2)—C(11)	1.827 (3)	C(12)—C(15)	1.533 (4)
N(1)—C(3)	1.477 (3)	C(16)—C(17)	1.537 (4)
N(1)—C(6)	1.465 (3)	C(17)—C(18)	1.534 (4)
N(2)—C(13)	1.470 (3)	C(17)—C(19)	1.533 (4)
N(2)—C(16)	1.476 (3)	C(17)—C(20)	1.547 (4)
(b) Angles (°)			
S(1)—Ag—S(2)	160.6 (1)	C(4)—C(2)—C(5)	108.6 (2)
S(1)—Ag—N(1)	90.0 (1)	N(1)—C(3)—C(2)	115.5 (2)
S(1)—Ag—N(2)	90.7 (1)	N(1)—C(6)—C(7)	115.5 (2)
S(1)—Ag—O(1)	98.0 (1)	C(6)—C(7)—C(8)	113.2 (2)
S(2)—Ag—N(1)	89.2 (1)	C(6)—C(7)—C(9)	109.9 (2)
S(2)—Ag—N(2)	90.2 (1)	C(6)—C(7)—C(10)	107.2 (2)
S(2)—Ag—O(1)	101.4 (1)	C(8)—C(7)—C(9)	107.3 (2)
N(1)—Ag—N(2)	179.3 (1)	C(8)—C(7)—C(10)	110.0 (2)
N(1)—Ag—O(1)	93.8 (1)	C(9)—C(7)—C(10)	109.1 (2)
N(2)—Ag—O(1)	86.1 (1)	S(2)—C(8)—C(7)	112.8 (2)
Ag—S(1)—C(1)	89.6 (1)	S(2)—C(11)—C(12)	113.1 (2)
Ag—S(1)—C(18)	88.6 (1)	C(11)—C(12)—C(13)	113.6 (2)
Ag—S(2)—C(8)	89.9 (1)	C(11)—C(12)—C(14)	110.0 (2)
Ag—S(2)—C(11)	89.0 (1)	C(11)—C(12)—C(15)	106.8 (2)
Ag—N(1)—C(3)	104.9 (2)	C(13)—C(12)—C(14)	106.8 (2)
Ag—N(1)—C(6)	106.5 (2)	C(13)—C(12)—C(15)	109.9 (2)
Ag—N(2)—C(13)	107.7 (2)	C(14)—C(12)—C(15)	109.7 (2)
Ag—N(2)—C(16)	106.5 (1)	N(2)—C(13)—C(12)	115.6 (2)
Ag—O(1)—C(21)	130.9 (2)	N(2)—C(16)—C(17)	115.2 (2)
C(1)—S(1)—C(18)	100.5 (1)	C(16)—C(17)—C(18)	114.2 (2)
C(8)—S(2)—C(11)	99.1 (1)	C(16)—C(17)—C(19)	110.6 (2)
C(3)—N(1)—C(6)	109.8 (2)	C(16)—C(17)—C(20)	107.2 (2)
C(13)—N(2)—C(16)	110.6 (2)	C(18)—C(17)—C(19)	106.6 (2)
S(1)—C(1)—C(2)	112.2 (2)	C(18)—C(17)—C(20)	109.8 (2)
C(1)—C(2)—C(3)	113.5 (2)	C(19)—C(17)—C(20)	108.4 (2)
C(1)—C(2)—C(4)	107.7 (2)	S(1)—C(18)—C(17)	112.6 (2)
C(1)—C(2)—C(5)	109.5 (2)	O(1)—C(21)—O(2)	124.3 (3)
C(3)—C(2)—C(4)	110.0 (2)	O(1)—C(21)—C(22)	118.2 (3)
C(3)—C(2)—C(5)	107.4 (2)	O(2)—C(21)—C(22)	117.5 (3)

in 1-oxa-7,10-dithia-4,13-diazacyclopentadecanesilver(I) thiocyanate (Louis & Weiss, 1976), and Ag—S 2.555–2.600 (4) and Ag—N 2.317–2.537 (10) Å in a 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo-[14.3.1]icosane-1(20),2,14,16,18-pentaenesilver(I) salt (Drew, Cairns, McFall & Nelson, 1980). The Ag—O distance [2.686 (2) Å] is much longer than other Ag—O bond lengths in carboxylsilver(I) structures such as [Ag₂(C₅H₅N)₂(C₆H₅CO₂)₂] (Hedrich & Hartl, 1983) where Ag—O distances of 2.27–2.53 (1) Å are found with four-coordinate silver, in [HAg{C₆H₄(NH₂)SO₂-NHCH₂CO₂}₂] (Ray & Saha, 1978) with Ag—O 2.60 (1) Å, and in [Ag₂(NH₃CH₂CO₂)₂](NO₃)₂ (Rao & Viswamitra, 1972) with Ag—O 2.22 and 2.25 (1) Å and longer contacts of 2.37–2.86 Å. The remaining bond lengths in the complex are in accord with expected values [mean S—C 1.826 (3), mean N—C 1.472 (3), mean C—C 1.537 (4) Å]. The angles Ag—S—C [mean

89.3 (1°) and Ag–N–C [mean 106.4 (2)°] follow the same trend as found in other metal complexes with the same ligand *L*, e.g. Pd–S–C 102.0 (7), Pd–N–C 116.9 (13)° in [PdL]Cl₂·2H₂O (Ferguson, McCrindle, McAlees, Parvez & Stephenson, 1983) and Cu–S–C 99.2 (7), Cu–N–C 105.8 (9)° in [CuL]Cl₂ (Ferguson, McCrindle & Parvez, 1984).

In the solid, the orientation of the CH₃CO₂ ligand is determined by an intramolecular N(2)–H···O(2) hydrogen bond with N···O 3.037 (3) Å. The water molecules are hydrogen-bonded to the complex molecule as shown in Fig. 3. Water oxygen O(3) hydrogen-bonds to carboxyl oxygen O(1), to water molecule O(4)', and to N(1), *via* O(3)–H···O(1) [O···O 2.712 (3) Å], O(3)–H···O(4)' [O···O 2.975 (4) Å] and O(3)···H–N(1) [O···N 3.228 (3) Å] hydrogen bonds. Water molecule O(4) is hydrogen-bonded to acetato oxygen O(2) [O(4)–H···O(2), O···O 2.760 (3) Å]. In this way a centrosymmetric dimer is established with a 16-membered hydrogen-bonded ring system. The dimers are in turn linked through the O(4) water molecules, about inversion centres, to produce an infinite chain along the *a* direction. The O(4)···O(4)'' distance, 2.960 (6) Å, is consistent with such a hydrogen-bond assignment. The only H atom which did not appear clearly on our difference maps was the second one bonded to O(4) and is presumably disordered and involved in the interdimer hydrogen bonding. The 0.3 e Å⁻³ maxima found in our final difference map were all in the volume between O(4) and O(4)'.

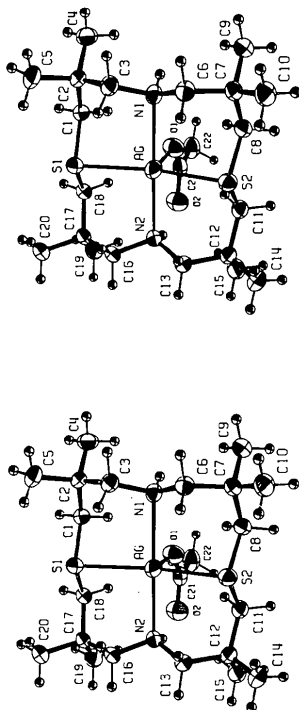


Fig. 1. A stereoview of the molecule (2) with the crystallographic numbering scheme.

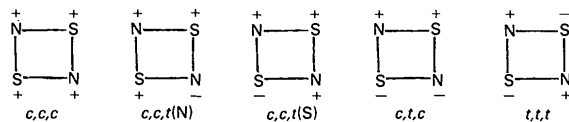


Fig. 2. The five possible configurations of the macrocycle when acting as a tetradentate ligand; the positive and negative signs denote the relative orientation of the NH protons and the S lone pairs with respect to the ring plane.

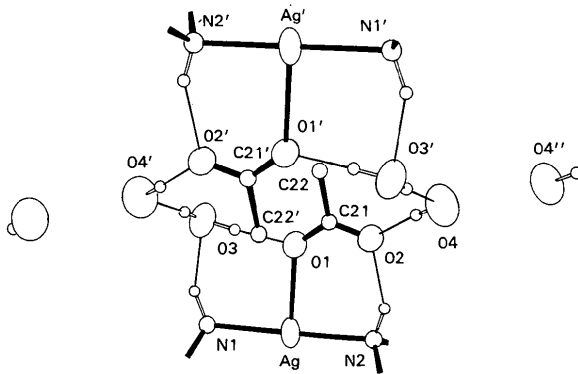


Fig. 3. Schematic representation of the hydrogen-bonded structure of (2)·2H₂O extended along the *a* axis. Only those parts of the molecule of (2) are drawn which participate in hydrogen bonds.

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