

0.047 (5) Å with a maximum deviation of 0.059 (5) Å, again for C(4). The benzene ring shows no significant deviation from planarity, the r.m.s. deviation being 0.007 (6) Å. The dihedral angle between the two five-membered rings is 116.6 (4)° and that between the five- and six-membered rings is 175.6 (5)°. The packing is shown in Fig. 2.

This work was supported in part by a grant from the Epilepsy Foundation of America.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC Crystallographic Programs for the IBM/360 System. Accession Nos. 133–147 in *J. Appl. Cryst.* **6**, 324–325.
 ALEXANDER, G. J. & CHATTERJIE, N. (1980). *Res. Commun. Chem. Pathol. Pharmacol.* **27**, 45–56.
 ARENS, A., GRUNSBERGS, F. & JURGEVICA, I. (1974). *Khim. Geterotsikl. Soedin.* **4**, 549–551.

- CHATTERJIE, N., SINHA, B. & ALEXANDER, G. J. (1983). *Res. Commun. Chem. Pathol. Pharmacol.* **39**, 333–336.
 CROOKS, P. A. & DEEKS, T. (1975). *Chem. Ind. (London)*, pp. 793–794.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–214. Birmingham: Kynoch Press.
 LAHDESMAKI, P. & OJA, S. S. (1973). *J. Neurochem.* **20**, 1411–1417.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MUTANI, R., BERGAMINI, L. & DURELLI, L. (1978). *Taurine and Neurological Disorders*, edited by A. BARBEAU & R. J. HUXTABLE, pp. 359–373. New York: Raven Press.
 OJA, S. S., KONTRO, P., LINDEN, I. B., ANDERSEN, L. & GOTHONI, G. (1982). *Acta Neurol. Scand. Suppl.* **90**, 65: 188.
 SALKOWSKI, E. (1973). *Ber. Dtsch. Chem. Ges.* **6**, 744–776, 1191–1193.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1984). **C40**, 350–354

Nitratopentakis(thiourea)bismuth(III) Nitrate Monohydrate, [Bi(NO₃)₅{SC(NH₂)₂}₅](NO₃)₂·H₂O, and Trinitratotrakis(thiourea)bismuth(III), [Bi(NO₃)₃{SC(NH₂)₂}₃]

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(Received 10 April 1983; accepted 3 October 1983)

Abstract. [Bi(NO₃)₅{SC(NH₂)₂}₅](NO₃)₂·H₂O: *M_r* = 793.61, red, triclinic, *P* $\bar{1}$, *a* = 9.292 (1), *b* = 9.788 (1), *c* = 15.729 (1) Å, α = 118.55 (1), β = 92.99 (1), γ = 93.72 (1)°, *V* = 1248.3 Å³, *Z* = 2, *D_m* = 2.12 (1), *D_x* = 2.11 Mg m⁻³, Mo *K*α radiation, λ = 0.7107 Å, μ = 7.056 mm⁻¹, *T* = 295 K, *F*(000) = 772, *R*(*F*) = 0.039, *R_w*(*F*) = 0.039 [5300 data in the range 0.0467 < (sin θ)/ λ < 0.7049 Å⁻¹ with *F_o*² > 3σ(*F_o*²)]; Bi–S 2.637 (2)–2.937 (2) Å; Bi–O 2.814 (5) and 2.916 (5) Å. [Bi(NO₃)₃{SC(NH₂)₂}₃]: *M_r* = 623.36, yellow, monoclinic, *P*2₁/*c*, *a* = 6.9556 (9), *b* = 15.801 (3), *c* = 15.561 (2) Å, β = 91.87 (1)°, *V* = 1709.3 Å³, *Z* = 4, *D_m* = 2.422 (5), *D_x* = 2.421 Mg m⁻³, Mo *K*α radiation, λ = 0.7107 Å, μ = 10.692 mm⁻¹, *T* = 295 K, *F*(000) = 1184, *R*(*F*) = 0.042, *R_w*(*F*) = 0.047 [3263 data in the range

0.0443 < (sin θ)/ λ < 0.5958 Å⁻¹ with *F_o*² > 3σ(*F_o*²)]; Bi–S 2.668 (3)–2.681 (3) Å; Bi–O 2.579 (9)–2.94 (1) Å (two bridging NO₃ groups). Extensive hydrogen bonding and probable C···N π-donor–π-acceptor interaction occur for both structures.

Introduction. In the course of a systematic investigation into the interaction of thiourea with Bi^{III} salts, the title compounds were isolated. In order to understand the solid-state thermal decomposition of these species it became necessary to determine their crystal and molecular structures. The compounds were prepared by slow evaporation of solutions containing Bi(NO₃)₃ and thiourea. The product composition was controlled by thiourea concentration.

Experimental. $[\text{Bi}(\text{NO}_3)\{\text{SC}(\text{NH}_2)_2\}_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. Preliminary precession and Weissenberg photographs showed triclinic symmetry. Picker FACS-I diffractometer. Lattice parameters and crystal orientation determined by least-squares refinement of 23 automatically centered reflections with $0.3670 < (\sin\theta)/\lambda < 0.4093 \text{ \AA}^{-1}$. Other details in Table 1. Six standard reflections: linear isotropic decrease 6%. Lorentz, polarization, decomposition and absorption corrections. All calculations with a modification of the Northwestern University Crystallographic Computing Library (Waters & Ibers, 1977). Structure solved using Patterson methods, and all refinements assumed space group $P\bar{1}$. Most H atoms located. All except those on the water molecule included at their calculated idealized positions (N—H 0.95 Å, planar thiourea group) with temperature factors $B_{\text{H}} = B_{\text{N}} + 1.0 \text{ \AA}^2$ as fixed contribution to F . All other atoms refined anisotropically using the unique data for which $F_o^2 > 3\sigma(F_o^2)$. At convergence $(\Delta/\sigma)_{\text{max}} < 0.10$. A parameter for secondary extinction was also refined [final value $9.9 (6) \times 10^{-7}$]. The weighting scheme (Table 1) showed no dependence of the function minimized upon the magnitude of F_o and $(\sin\theta)/\lambda$. Final difference Fourier map featureless with the highest peaks ($< 1.2 \text{ e \AA}^{-3}$) in the vicinity of the Bi atom.

$[\text{Bi}(\text{NO}_3)_3\{\text{SC}(\text{NH}_2)_2\}_3]$. Preliminary precession and Weissenberg photographs established monoclinic symmetry and systematic absences consistent with the space group $P2_1/c$. Lattice parameters determined by least-squares refinement of the setting angles of 19 automatically centered reflections with $0.3411 < (\sin\theta)/\lambda < 0.3886 \text{ \AA}^{-1}$. Other details in Table 1. Six standard reflections showed no trends. Lorentz, polarization and absorption corrections. Structure solved by Patterson methods. H atoms included at the calculated idealized positions as before, and not refined. All other atoms refined anisotropically using the unique data for which $F_o^2 > 3\sigma(F_o^2)$. A variable parameter for secondary extinction was included [final value

Table 1. *Data-collection parameters*

	Red compound	Yellow compound
Crystal shape	Parallelepiped	Flattened cuboid,
	$0.20 \times 0.16 \times 0.11 \text{ mm}$	$0.21 \times 0.19 \times 0.14 \text{ mm}$
Crystal volume	0.0045 mm^3	0.0050 mm^3
Transmission factors	0.309–0.437	0.117–0.276
Scan speed	$2.0^\circ (2\theta) \text{ min}^{-1}$	$2.0^\circ (2\theta) \text{ min}^{-1}$
Background counts	10s with rescans option*	10s with rescans option*
Scan range	1.0° below $K\alpha_1$ to 0.9° above $K\alpha_2$	1.0° below $K\alpha_1$ to 0.9° above $K\alpha_2$
Data collected	$\pm h, \pm k, l$	$\pm h, k, l$
ρ^\dagger	0.03	0.03
Number of reflections measured	6875	3263

* Lenhart (1975).

† Used in the calculation of $\sigma(F_o^2)$ for optimal weighting: $\sigma_I^2 = \sigma_{\text{counting}}^2 + (pI)^2$ where I is the intensity corrected only for background and attenuator factors.

Table 2. *Final positional parameters and isotropic thermal parameters for non-hydrogen atoms of $[\text{Bi}(\text{NO}_3)\{\text{SC}(\text{NH}_2)_2\}_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$*

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The isotropic thermal parameter is from the last cycle of isotropic refinement before correction for absorption was made.

	x	y	z	$B(\text{Å}^2)$
Bi	-0.22869 (3)	0.07278 (3)	0.22066 (2)	2.00 (2)
S(1)	0.4825 (2)	0.0238 (2)	0.1511 (1)	3.03 (9)
S(2)	-0.1789 (2)	0.0589 (2)	0.0481 (1)	3.7 (1)
S(3)	0.0761 (2)	0.0524 (2)	0.2604 (1)	3.8 (1)
S(4)	-0.2971 (2)	0.0209 (3)	0.3839 (1)	4.7 (1)
S(5)	-0.2426 (2)	-0.2302 (2)	0.1002 (1)	3.5 (1)
C(1)	0.4446 (6)	0.2046 (7)	0.1649 (5)	2.6 (3)
C(2)	-0.0692 (7)	0.2274 (8)	0.0775 (5)	3.0 (4)
C(3)	0.0946 (7)	0.1794 (8)	0.3848 (5)	3.6 (4)
C(4)	-0.4618 (8)	-0.0825 (9)	0.3696 (5)	3.8 (4)
C(5)	-0.2392 (7)	-0.3163 (7)	0.1746 (5)	3.1 (4)
N(11)	0.3990 (6)	0.3101 (7)	0.2468 (4)	3.7 (3)
N(12)	0.4542 (6)	0.2322 (6)	0.0915 (4)	3.5 (3)
N(21)	0.0449 (7)	0.2766 (7)	0.1424 (5)	4.3 (4)
N(22)	-0.0989 (7)	0.3040 (8)	0.0313 (5)	5.1 (4)
N(31)	0.1004 (7)	0.1219 (7)	0.4454 (4)	4.1 (4)
N(32)	0.1023 (7)	0.3333 (7)	0.4191 (5)	4.4 (4)
N(41)	-0.4724 (8)	-0.1763 (9)	0.4066 (6)	5.9 (4)
N(42)	-0.5805 (7)	-0.0687 (8)	0.3260 (5)	4.4 (4)
N(51)	-0.3544 (7)	-0.3935 (8)	0.1777 (5)	4.7 (4)
N(52)	-0.1173 (6)	-0.3090 (7)	0.2240 (5)	3.9 (3)
N(6)	0.2555 (6)	0.4499 (7)	0.3390 (5)	4.0 (4)
N(7)	0.2673 (6)	-0.4236 (6)	0.1177 (4)	3.7 (3)
N(8)	0.1554 (7)	-0.3423 (7)	0.3668 (4)	4.7 (4)
O(61)	-0.2608 (5)	0.3753 (6)	0.2491 (4)	4.1 (3)
O(62)	-0.2262 (7)	0.3841 (6)	0.3872 (4)	5.4 (4)
O(63)	-0.2807 (7)	0.5884 (6)	0.3795 (5)	6.5 (4)
O(71)	0.3526 (6)	-0.3594 (7)	0.0875 (5)	5.9 (4)
O(72)	0.3120 (6)	-0.4917 (6)	0.1610 (4)	5.0 (3)
O(73)	0.1352 (5)	-0.4238 (7)	0.1028 (4)	5.1 (3)
O(81)	0.1628 (6)	-0.2213 (6)	0.3591 (4)	4.6 (3)
O(82)	0.2676 (7)	-0.3964 (7)	0.3767 (5)	6.0 (3)
O(83)	0.0371 (8)	-0.4076 (9)	0.3644 (6)	6.0 (3)
O(9)	0.4663 (7)	0.3236 (8)	0.4376 (4)	7.9 (4)

Table 3. *Final positional parameters and isotropic thermal parameters for non-hydrogen atoms of $[\text{Bi}(\text{NO}_3)_3\{\text{SC}(\text{NH}_2)_2\}_3]$*

The isotropic thermal parameter is from the last cycle of isotropic refinement after correction for absorption was made.

	x	y	z	$B(\text{Å}^2)$
Bi	0.25092 (7)	0.18205 (3)	0.20865 (3)	1.21 (6)
S(1)	-0.0927 (5)	0.1609 (2)	0.1303 (2)	2.5 (3)
S(2)	0.0378 (5)	0.3102 (2)	0.2661 (2)	2.8 (3)
S(3)	0.4138 (5)	0.2762 (2)	0.0883 (2)	2.4 (2)
N(11)	-0.083 (1)	0.3110 (6)	0.0512 (7)	3.3 (8)
N(12)	-0.197 (2)	0.1984 (6)	-0.0291 (7)	3.4 (9)
N(21)	0.265 (2)	0.3308 (7)	0.4044 (7)	4.5 (10)
N(22)	0.151 (2)	0.4503 (7)	0.3406 (8)	5.2 (11)
N(31)	0.336 (2)	0.4380 (7)	0.0835 (8)	4.4 (10)
N(32)	0.508 (2)	0.3948 (7)	0.2027 (7)	3.9 (10)
N(4)	0.322 (2)	0.0174 (7)	0.0785 (7)	2.7 (8)
N(5)	0.131 (2)	0.0608 (8)	0.3624 (8)	3.8 (10)
N(6)	0.618 (2)	0.1433 (7)	0.3285 (7)	3.6 (9)
O(41)	0.353 (2)	0.0968 (5)	0.0764 (6)	4.5 (8)
O(42)	0.284 (2)	-0.0198 (6)	0.0105 (6)	5.8 (10)
O(43)	0.322 (2)	-0.0184 (7)	0.1473 (7)	7.4 (12)
O(51)	0.068 (2)	0.0574 (6)	0.2860 (6)	5.5 (9)
O(52)	0.212 (1)	0.1275 (7)	0.3877 (7)	4.7 (9)
O(53)	0.106 (2)	0.0017 (8)	0.4107 (8)	7.2 (12)
O(61)	0.561 (1)	0.0884 (5)	0.2776 (6)	3.6 (7)
O(62)	0.573 (1)	0.2193 (5)	0.3157 (6)	3.3 (7)
O(63)	0.721 (2)	0.1239 (7)	0.3932 (7)	5.6 (10)
C(1)	-0.117 (2)	0.2295 (8)	0.0440 (7)	1.4 (8)
C(2)	0.165 (2)	0.3681 (8)	0.3443 (8)	2.7 (10)
C(3)	0.418 (2)	0.3791 (8)	0.1279 (8)	2.7 (10)

Table 4. Bond distances (Å) for [Bi(NO₃)₃{SC(NH₂)₂}₃](NO₃)₂·H₂O

Bi—S(5)	2.637 (2)	C(3)—N(31)	1.318 (9)
Bi—S(2)	2.718 (2)	C(3)—N(32)	1.331 (9)
Bi—S(1)	2.767 (2)	C(4)—N(41)	1.303 (9)
Bi—S(3)	2.909 (2)	C(4)—N(42)	1.317 (9)
Bi—S(4)	2.937 (2)	C(5)—N(51)	1.286 (8)
Bi—O(61)	2.814 (5)	C(5)—N(52)	1.318 (8)
Bi—O(62)	2.916 (5)	N(6)—O(61)	1.239 (7)
S(1)—C(1)	1.739 (6)	N(6)—O(62)	1.238 (7)
S(2)—C(2)	1.725 (7)	N(6)—O(63)	1.237 (7)
S(3)—C(3)	1.736 (7)	N(7)—O(71)	1.227 (7)
S(4)—C(4)	1.721 (8)	N(7)—O(72)	1.233 (7)
S(5)—C(5)	1.739 (7)	N(7)—O(73)	1.238 (7)
C(1)—N(11)	1.321 (8)	N(8)—O(81)	1.244 (7)
C(1)—N(12)	1.312 (8)	N(8)—O(82)	1.235 (8)
C(2)—N(21)	1.323 (9)	N(8)—O(83)	1.225 (8)
C(2)—N(22)	1.302 (9)		

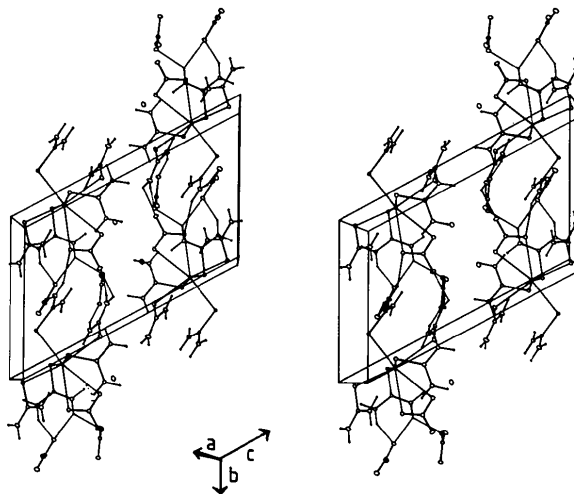


Fig. 2. Stereoscopic diagram of the contents of the unit cell for [Bi(NO₃)₃{SC(NH₂)₂}₃](NO₃)₂·H₂O. The hydrogen-bonding network is shown.

Table 5. Bond distances (Å) for [Bi(NO₃)₃{SC(NH₂)₂}₃]

Bi—S(1)	2.668 (3)	C(2)—N(21)	1.29 (1)
Bi—S(3)	2.672 (3)	C(2)—N(22)	1.30 (2)
Bi—S(2)	2.681 (3)	C(3)—N(31)	1.28 (1)
Bi—O(41)	2.579 (9)	C(3)—N(32)	1.32 (1)
Bi—O(51)	2.66 (1)	N(4)—O(41)	1.27 (1)
Bi—O(61)	2.799 (9)	N(4)—O(42)	1.23 (1)
Bi—O(62)	2.813 (8)	N(4)—O(43)	1.21 (1)
Bi—O(52)	2.94 (1)	N(5)—O(51)	1.25 (1)
S(1)—C(1)	1.73 (1)	N(5)—O(52)	1.25 (1)
S(2)—C(2)	1.74 (1)	N(5)—O(53)	1.21 (1)
S(3)—C(3)	1.74 (1)	N(6)—O(61)	1.23 (1)
C(1)—N(11)	1.31 (1)	N(6)—O(62)	1.25 (1)
C(1)—N(12)	1.34 (1)	N(6)—O(63)	1.24 (1)

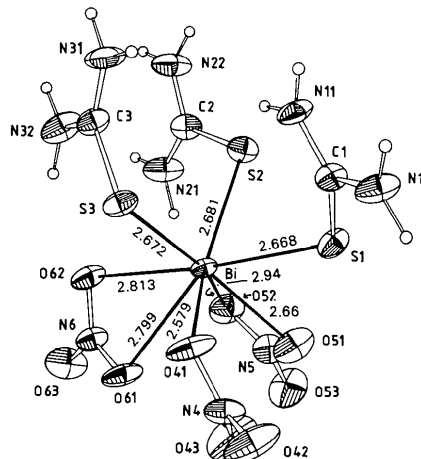


Fig. 3. ORTEP diagram of yellow [Bi(NO₃)₃{SC(NH₂)₂}₃]. Thermal ellipsoids are drawn at the 50% probability level; H atoms are shown artificially small. (Distances are in Å.)

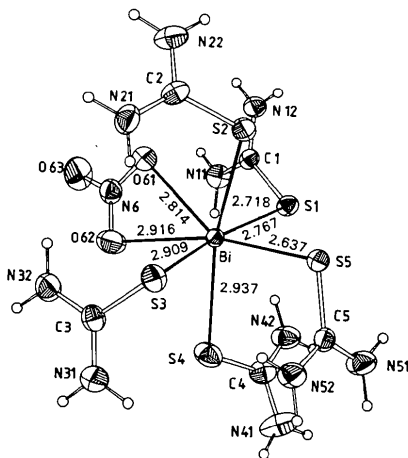


Fig. 1. ORTEP diagram (Johnson, 1965) of the red [Bi(NO₃)₃{SC(NH₂)₂}₃]²⁺ cation. Thermal ellipsoids are drawn at the 50% probability level; H atoms are shown artificially small. (Distances are in Å.)

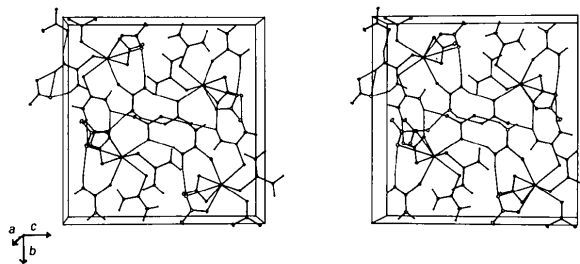


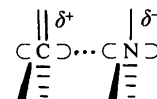
Fig. 4. Stereoscopic diagram of the contents of the unit cell for [Bi(NO₃)₃{SC(NH₂)₂}₃]. The hydrogen-bonding network is shown.

$6.4 (7) \times 10^{-7}$]. At convergence $(\Delta/\sigma)_{\max} = 0.15$. The weighting scheme (Table 1) showed only a slight dependence of the function minimized upon the magnitude of F_o and $(\sin\theta)/\lambda$ with low-angle intense data returning slightly higher values. Final difference Fourier synthesis rather noisy with the highest peaks ($1.95 \text{ e } \text{Å}^{-3}$) concentrated near the Bi atom. Crystal quality noticeably inferior to that for $[\text{Bi}(\text{NO}_3)\{\text{SC}(\text{NH}_2)_2\}_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. For both structures neutral-atom scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974), and the largest negative peaks in the final difference Fourier maps were of similar magnitude as the largest positive peaks.

Discussion. Final positional parameters for $[\text{Bi}(\text{NO}_3)\{\text{SC}(\text{NH}_2)_2\}_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{Bi}(\text{NO}_3)_3\{\text{SC}(\text{NH}_2)_2\}_3]$ are given in Tables 2 and 3 respectively.* Some metrical details for the red $[\text{Bi}(\text{NO}_3)\{\text{SC}(\text{NH}_2)_2\}_5](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ complex (I) are given in Table 4; others have been deposited. Fig. 1 depicts the cation: noteworthy is the curious manner in which thiourea ligands (4) and (5) are approximately parallel (dihedral angle 11.2°). Counting the bidentate nitrate group as a unit, the complex has approximate octahedral symmetry similar to that in a number of chloro compounds – for example: di- μ -chloro-tetrachlorotetrakis(thiourea-*S*)-dibismuth(III) species (Battaglia & Corradi, 1981); catena- μ -chloro-dichlorobis(ethylenethiourea)-bismuth(III) (Battaglia, Corradi, Nardelli & Tani, 1978); a $\text{BiCl}_3 \cdot 3[\text{SC}(\text{NH}_2)_2]$ species (Battaglia, Corradi, Pelizzi & Tani, 1977); and a di- μ -chloro-bis[chlorotris(thiourea)bismuth(III)] pentachloro(thiourea)bismuthate(III) (Battaglia, Corradi, Pelizzi & Tani, 1975). A hexakis(thiourea) Bi^{III} trinitrate complex has also been fully characterized (Battaglia & Corradi, 1981). The two long Bi–S bonds in the red complex (I) are notably longer than those observed in other Bi^{III} thiourea complexes (typically 2.71 Å). The stereochemistry of the thiourea groups for (I) is similar to previous observations (see above references). The Bi–S–C angles are in the range $98.6 (2)–115.8 (3)^\circ$. Crystal packing is illustrated in Fig. 2.

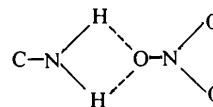
Bond distances for the yellow $[\text{Bi}(\text{NO}_3)_3\{\text{SC}(\text{NH}_2)_2\}_3]$ complex (II) are given in Table 5, while Fig. 3 illustrates the molecular stereochemistry. In contrast to (I), the Bi is octacoordinated; when bidentate nitrate groups are counted as a unit, approximately octahedral coordination with three mutually *cis* thiourea groups

pertains. The Bi–S bond lengths are short by comparison with other related complexes. The Bi–S–C bond angles fall in the range $105.9 (4)–110.9 (4)^\circ$. Again a curious stacking of the thiourea ligands occurs: dihedral angle between the planes formed by groups (1) and (2) is 22.4° , between groups (1) and (3) 24.0° , and between groups (2) and (3) 10.9° . We believe that this arrangement facilitates weak intramolecular π -donor– π -acceptor interaction:



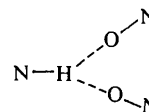
The intramolecular C(2)···N(32) separation is $3.33 (2) \text{ Å}$. Similarly, for complex (I) there is a C(4)···N(51) separation of $3.361 (10) \text{ Å}$, and also an S(4)···C(5) separation of $3.471 (7) \text{ Å}$.

The crystal packing for (II) is illustrated in Fig. 4. In both complexes evidence for an intermolecular π -donor– π -acceptor interaction can be found: for (I) the parallel groups (4) maintain a C(4)···N(41) separation of $3.330 (11) \text{ Å}$, and for (II) the approximately parallel groups (2) and (1) maintain a C(2)···N(12) separation of $3.41 (2) \text{ Å}$. In addition, in both structures there are extensive hydrogen-bonding networks linking N–H moieties with nitrate O atoms. For (I) there are 17 N···O separations in the range $2.835 (7)–3.154 (8) \text{ Å}$, and N–H···O angles in the range $113–167^\circ$. It should be borne in mind that H-atom parameters are idealized. An eighteenth separation N(22)···O(73)' is short at $2.877 (9) \text{ Å}$ but the



arrangement leads to angles of 100° . The water molecule bridges a thiourea to a nitrate group.

For the yellow complex (II) there are nine separations in the range $2.904 (13)–3.243 (14) \text{ Å}$ with associated N–H···O angles in the range $123–168^\circ$. Two other N···O separations at $2.925 (14)$ and $3.136 (13) \text{ Å}$ involve a common H atom.



* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles, least-squares planes and dihedral angles, and H-bonding details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38947 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The support of the Swiss National Science Foundation is gratefully acknowledged.

References

- BATTAGLIA, L. P. & CORRADI, A. B. (1981). *J. Chem. Soc. Dalton Trans.* pp. 23–26.
 BATTAGLIA, L. P., CORRADI, A. B., NARDELLI, M. & TANI, M. E. V. (1978). *J. Chem. Soc. Dalton Trans.* pp. 583–587.
 BATTAGLIA, L. P., CORRADI, A. B., PELIZZI, G. & TANI, M. E. V. (1975). *Cryst. Struct. Commun.* **4**, 399–402.

- BATTAGLIA, L. P., CORRADI, A. B., PELIZZI, G. & TANI, M. E. V. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1141–1144.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 LENHART, P. G. (1975). *J. Appl. Cryst.* **8**, 968–970.
 WATERS, J. M. & IBERS, J. A. (1977). *Inorg. Chem.* **16**, 3273–3277.

Acta Cryst. (1984). **C40**, 354–356

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

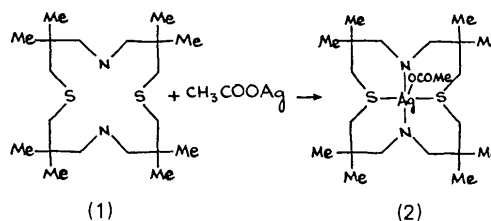
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(Received 3 August 1983; accepted 17 October 1983)

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).