CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
FRIES, D. C., RAO, S. T. & SUNDARALINGAM, M. (1971). *Acta Cryst.* B**27**, 994–1005.
GRESS, M. E. & JEFFREY, G. A. (1977). *Acta Cryst.* B**33**, 2490–2495.
JEFFREY, G. A., GRESS, M. E. & TAKAGI, S. (1977). *J. Am. Chem. Soc.* **99**, 609–611.
JEFFREY, G. A., MCMULLAN, R. K. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 728–737.
JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1972). *Carbohydr. Res.* **25**, 117–131.
JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.
JEFFREY, G. A. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 738–742.
KANTERS, J. A., GAYKEMA, W. P. J. & ROELOFSEN, G. (1978). *Acta Cryst.* B**34**, 1873–1881.
KILLEAN, R. C. G., LAWRENCE, J. L. & SHARMA, V. C. (1971). *Acta Cryst.* B**27**, 1707–1710.
LONGCHAMBON, F., OHANESSIAN, J., AVENEL, D. & NEUMAN, A. (1975). *Acta Cryst.* B**31**, 2623–2627.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.
STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.
TAKAGI, S. & JEFFREY, G. A. (1977). *Acta Cryst.* B**33**, 3033–3040.
TAKUSAGAWA, F. & JACOBSON, R. A. (1978). *Acta Cryst.* B**34**, 213–218.
TSE, Y.-C. & NEWTON, M. D. (1977). *J. Am. Chem. Soc.* **99**, 611–613.
WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

Acta Cryst. (1978). B**34**, 3053–3056

Preparation and X-ray Analysis of a 1:1 Adduct of Hexamethylenetetramine Oxide and Thiourea

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A 1:1 adduct of hexamethylenetetramine oxide and thiourea ($C_6H_{12}N_4O.CH_4N_2S$) has been prepared and subjected to crystal-structure analysis. The crystals are orthorhombic, space group *Pbca*, with $a = 7{\cdot}698$ (5), $b = 12{\cdot}03$ (1), $c = 23{\cdot}09$ (2) Å and $Z = 8$. The structure was solved by direct methods and refined with 1426 observed Cu $K\alpha$ film data to $R = 0{\cdot}099$. In the crystal lattice each $(CH_2)_6N_4O$ molecule is linked by O···H–N hydrogen bonds to three thiourea molecules and *vice versa*, giving rise to corrugated layers normal to **c**. Neighboring layers, related by the *c* glide, pack with protruding $(CH_2)_6N_4$ groups fitting into hollows between the layers.

Introduction

X-ray analysis of the 1:2 adduct of hexamethylenetetramine with thiourea, $(CH_2)_6N_4.2(NH_2)_2CS$, has shown that the two molecular components are linked by N···H–N and S···H–N hydrogen bonds in a three-dimensional network (Mak, Lau, Ladd & Povey, 1978). Recently we isolated hexamethylenetetramine oxide, $(CH_2)_6N_4O$, and a number of its acid adducts (Lam & Mak, 1978*a*). The title compound was prepared and studied as part of our current structural investigation of hydrogen-bonded molecular complexes of hexamethylenetetramine (Mak, Tse, Chong & Mok, 1977; Mak, Yu & Lam, 1978) and its *N*-oxide (Lam & Mak, 1978*b*; Mak & Lam, 1978).

Experimental

Preparation of the hexamethylenetetramine oxide–thiourea 1:1 adduct

Hexamethylenetetramine oxide (I) was prepared by the reaction of hexamethylenetetramine with 30% aqueous hydrogen peroxide (Lam & Mak, 1978*a*) and recrystallized from chloroform. Thiourea (II) was recrystallized from ethanol. Compounds (I) (0·8 g, 5 mmol) and (II) (0·4 g, 5 mmol) were dissolved separately in the minimum amount of ethanol. The solutions were mixed at room temperature and set aside for crystallization; these yielded colorless, air-stable crystals (III) of stoichiometry $C_7H_{16}N_6OS$† [m.p. 153–

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† Elemental analysis performed by the Australian Microanalytical Service, CSIRO, Parkville, Victoria, Australia.

155 °C (in sealed tube)]. The IR (KBr disc) spectrum of (III) consisted essentially of a superposition of the spectra of (I) and (II), except that the N—H stretching bands from (II) at 3380 and 3260 cm^{-1} shifted to 3350 and 3250 cm^{-1} respectively, and additional peaks at 730 cm^{-1} (sharp) and 535 cm^{-1} (broad) appeared in the spectrum of the adduct. The NMR spectrum of (III) in CD_3OD displayed two sets of methylene protons at δ 4·60 and 4·44 (broad) in the ratio 1:1. With $(CD_3)_2SO$ as solvent, these proton signals gave barely resolved peaks at δ 4·35 and 4·29, and a broad NH_2 peak appeared at δ 7·1. In $(CD_3)_2SO$, the protons of (I) were found at δ 4·54 and 4·33 (broad), and those of (II) at δ 7·1.

Samples suitable for X-ray study were crystallized from a methanol/ethanol mixture in the form of colorless plates. Accurate cell dimensions were determined from high-angle reflections on all three zero-layer Weissenberg photographs calibrated with NaCl powder lines and were refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$.

Crystal data

$(CH_2)_6N_4O.(NH_2)_2CS$, M_r = 232·31, m.p. 153–155 °C, orthorhombic, space group *Pbca*, a = 7·698 (5), b = 12·03 (1), c = 23·09 (2) Å, V = 2138 Å^3, Z = 8, D_m = 1·452 (5) (by flotation in CCl_4/benzene), D_x = 1·443 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 25·6 cm^{-1}.

A crystal of dimensions 0·3 × 0·3 × 0·4 mm was used to collect intensity data for $0kl$–$7kl$ and $h0l$–$h11l$ reflections by the multiple-film equi-inclination Weissenberg method with Cu $K\alpha$ radiation. The visually estimated intensities were corrected for Lorentz and polarization factors but absorption was ignored. A set of scaled structure amplitudes was derived (Hamilton, Rollett & Sparks, 1965), which, after reduction, consisted of 1426 independent observed and 908 unobserved reflections.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

	x	y	z
O(1)	0·4542 (5)	0·0948 (3)	0·1921 (2)
N(1)	0·3647 (6)	0·1040 (4)	0·1400 (2)
N(2)	0·1512 (8)	0·0184 (5)	0·0753 (2)
N(3)	0·3979 (7)	0·1230 (4)	0·0354 (2)
N(4)	0·1644 (7)	0·2228 (4)	0·0851 (2)
C(1)	0·2450 (9)	0·0051 (5)	0·1294 (3)
C(2)	0·4926 (8)	0·1094 (5)	0·0902 (3)
C(3)	0·2564 (8)	0·2079 (5)	0·1403 (3)
C(4)	0·2774 (10)	0·0261 (6)	0·0275 (3)
C(5)	0·2953 (9)	0·2258 (6)	0·0387 (3)
C(6)	0·0506 (9)	0·1235 (7)	0·0770 (4)
S(1)	0·6938 (2)	0·3761 (1)	0·1437 (1)
C(7)	0·8145 (7)	0·3150 (5)	0·1960 (2)
N(5)	0·7877 (7)	0·2077 (4)	0·2116 (2)
N(6)	0·9418 (7)	0·3717 (5)	0·2242 (2)

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix isotropic and anisotropic least-squares refinement of all 15 non-hydrogen atoms yielded R = 0·107. The positions of all methylene and amido H atoms were then generated with the program *GHMC* (Mak, Mok & Tse, 1977). Inclusion of these with B = 5·0 Å^2 give a final R of 0·099 and a featureless difference map.

Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and those for H from Stewart, Davidson & Simpson (1965). Computations were performed on an ICL-1904A system with *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, the weighting scheme being that of Cruickshank (1961) with $w = (2F_{\rm min} + |F_o| + 2|F_o|^2/F_{\rm max})^{-1}$, where $F_{\rm min}$ and $F_{\rm max}$ were 4·0 and 250·0 respectively.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

(*a*) Hexamethylenetetramine oxide			
O(1)—N(1)	1·391 (6)		
N(1)—C(1)	1·525 (8)	N(2)—C(4)	1·473 (9)
N(1)—C(2)	1·515 (8)	N(2)—C(6)	1·483 (10)
N(1)—C(3)	1·502 (8)	N(3)—C(4)	1·501 (9)
N(2)—C(1)	1·452 (9)	N(3)—C(5)	1·469 (9)
N(3)—C(2)	1·469 (8)	N(4)—C(5)	1·471 (9)
N(4)—C(3)	1·469 (8)	N(4)—C(6)	1·493 (9)
Around quaternary N atom (average O—N—C = 110·5, C—N—C = 108·4)			
O(1)—N(1)—C(1)	112·1 (4)	C(1)—N(1)—C(2)	107·7 (5)
O(1)—N(1)—C(2)	109·8 (4)	C(1)—N(1)—C(3)	108·3 (5)
O(1)—N(1)—C(3)	109·7 (4)	C(2)—N(1)—C(3)	109·2 (5)
Around tertiary N atoms (average C—N—C = 108·5)			
C(1)—N(2)—C(4)	108·9 (6)	C(4)—N(3)—C(5)	109·1 (5)
C(1)—N(2)—C(6)	109·3 (5)	C(3)—N(4)—C(5)	107·7 (5)
C(4)—N(2)—C(6)	108·1 (6)	C(3)—N(4)—C(6)	107·1 (5)
C(2)—N(3)—C(4)	109·0 (5)	C(5)—N(4)—C(6)	109·3 (5)
C(2)—N(3)—C(5)	108·4 (5)		
Around methylene C atoms (average N—C—N = 111·4)			
N(1)—C(1)—N(2)	110·7 (5)	N(2)—C(4)—N(3)	111·4 (5)
N(1)—C(2)—N(3)	109·6 (5)	N(3)—C(5)—N(4)	112·7 (5)
N(1)—C(3)—N(4)	111·4 (5)	N(2)—C(6)—N(4)	112·3 (5)
(*b*) Thiourea			
S(1)—C(7)	1·692 (6)	S(1)—C(7)—N(5)	121·3 (4)
N(5)—C(7)	1·356 (8)	S(1)—C(7)—N(6)	121·3 (4)
N(6)—C(7)	1·360 (8)	N(5)—C(7)—N(6)	117·4 (5)
(*c*) Hydrogen bonds			
O(1)···N(5)	2·939 (7)	O(1)···N(5)—C(7)	122·2 (4)
O(1)···N(5)$^{\rm i}$	2·904 (7)	O(1)···N(5)$^{\rm i}$—C(7)$^{\rm i}$	125·6 (4)
O(1)···N(6)$^{\rm ii}$	2·897 (7)	O(1)···N(6)$^{\rm ii}$—C(7)$^{\rm ii}$	122·8 (4)
N(1)—O(1)···N(5)	121·9 (3)		
N(1)—O(1)···N(5)$^{\rm i}$	114·0 (3)		
N(1)—O(1)···N(6)$^{\rm ii}$	115·6 (3)		

Roman numerals refer to the following equivalent positions relative to the atom at x,y,z: (i) $-\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $1\frac{1}{2} - x, -\frac{1}{2} + y, z$.

The final atomic parameters are listed in Table 1.* The atom numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. A *PLUTO* (Motherwell, 1976) stereoplot of the molecular packing is shown in Fig. 3.

Discussion

The dimensions of the two molecular components in $(CH_2)_6N_4O.(NH_2)_2CS$ (Table 2) are in good agreement with corresponding values in orthorhombic thiourea (Truter, 1967; Elcombe & Taylor, 1968) and other molecular complexes of hexamethylenetetramine oxide (Lam & Mak, 1978*b*; Mak & Lam, 1978). The thiourea molecule is planar within experimental error. The equation of the least-squares plane through S(1), C(7), N(5) and N(6) is $-0{\cdot}6619\,X - 0{\cdot}2964\,Y - 0{\cdot}6885Z = -0{\cdot}0898$, where X, Y and Z are Cartesian coordinates in Å referred to the cell axes. Attachment of an O atom to the $(CH_2)_6N_4$ skeleton causes a drastic modification of the cage geometry. The three types of C—N bonds disposed differently with respect to the *N*-oxide functional group are markedly different. Moving away from the quaternary N atom, the C—N bonds vary in the order long–short–normal (Table 2) relative to the observed length in crystalline $(CH_2)_6N_4$ (Becka & Cruickshank, 1963). A similar perturbation of ring geometry, in the form of bond alternation, by an exocyclic O atom has been observed for *cyclo*-heptasulfur oxide (Steudel, Reinhardt & Sandow, 1977) and *cyclo*-octasulfur oxide (Luger, Bradaczek, Steudel & Rebsch, 1976).

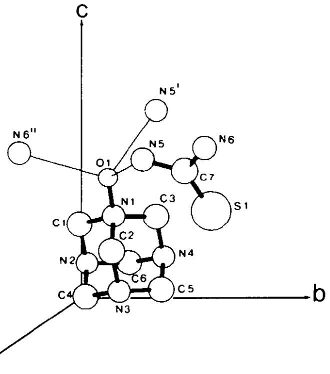

Fig. 1. Atom numbering in hexamethylenetetramine oxide–thiourea (1:1). Superscripts refer to the equivalent positions given in Table 2.

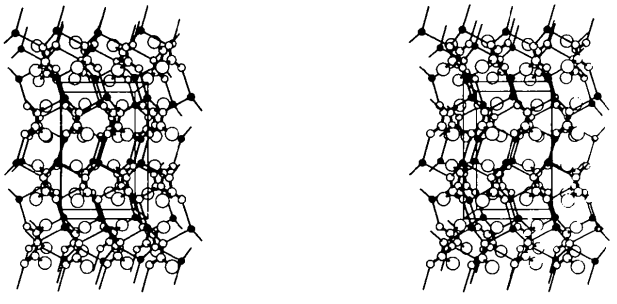

Fig. 2. Stereodrawing of three consecutive hydrogen-bonded layers viewed along **c**. The O atoms are shaded, and the protruding $(CH_2)_6N_4$ groups have been omitted for the sake of clarity.

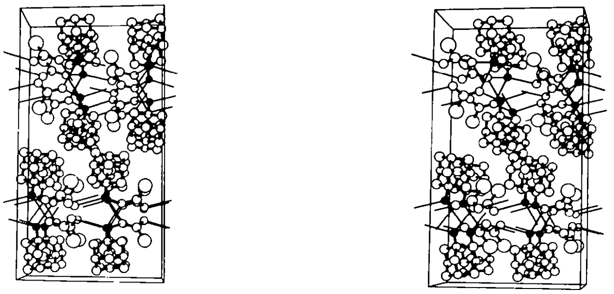

Fig. 3. Stereodrawing showing the molecular packing viewed approximately along **a** towards the origin of the unit cell at the lower left corner. The O atoms are shaded.

In the present adduct, the O atom and NH_2 groups are connected by O···H—N hydrogen bonds to form corrugated layers normal to **c**. Neighboring layers are related by the *c* glide, and a stereoview of the stacking of three consecutive hydrogen-bonded layers is shown in Fig. 2. The $(CH_2)_6N_4$ groups project from both sides of each layer and fill the space between neighboring layers (Fig. 3). In the hydrogen-bonding scheme, O(1) of the $(CH_2)_6N_4O$ molecule makes use of all three lone pairs in accepting protons from three thiourea molecules, but none of the three tertiary N atoms is involved. In turn, each thiourea molecule is hydrogen-bonded to the O atoms of three neighboring $(CH_2)_6N_4O$ molecules. If sp^2 hybridization is assumed for the amido N atoms, then all three O···H—N hydrogen bonds are within 6° of being linear (Table 2). Although the remaining N—H bond in each thiourea molecule appears to point towards the S atom of another thiourea molecule (Fig. 2), detailed consideration shows that the N(6)—H···S(1) system fails to meet accepted geometrical criteria for hydrogen bonding involving N and S (Donohue, 1969).

The present structure is similar in many ways to that of $(CH_2)_6N_4O.H_2O_2.H_2O$ (Mak & Lam, 1978). Both are characterized by a stacking of hydrogen-bonded layers normal to **c** and related by the *c* glide normal to **b**. For the $(CH_2)_6N_4O$ molecule in either adduct, hydrogen bonding occurs exclusively at the formally negative O atom, so that the $(CH_2)_6N_4$ moiety is relegated to a space-filling role. This situation is in

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* Lists of structure factors, anisotropic temperature factors, and generated hydrogen positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33600 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

marked contrast to that in $(CH_2)_6N_4.2(NH_2)_2CS$ (Mak, Lau, Ladd & Povey, 1978), in which all four tertiary N atoms are involved in the hydrogen-bond network.

References

Becka, L. N. & Cruickshank, D. W. J. (1963). *Proc. R. Soc. London Ser. A*, **273**, 435–454.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Cruickshank, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. Pepinsky, J. M. Robertson & J. C. Speakman, p. 45. Oxford: Pergamon Press.

Donohue, J. (1969). *J. Mol. Biol.* **45**, 231–235.

Elcombe, M. M. & Taylor, J. C. (1968). *Acta Cryst.* A**24**, 410–420.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hamilton, W. C., Rollett, J. S. & Sparks, R. S. (1965). *Acta Cryst.* **18**, 129–130.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Lam, Y.-S. & Mak, T. C. W. (1978*a*). *Aust. J. Chem.* **31**. In the press.

Lam, Y.-S. & Mak, T. C. W. (1978*b*). *Acta Cryst.* B**34**, 1915–1918.

Luger, P., Bradaczek, H., Steudel, R. & Rebsch, M. (1976). *Chem. Ber.* **109**, 180–184.

Mak, T. C. W. & Lam, Y.-S. (1978). *Acta Cryst.* B**34**, 1732–1735.

Mak, T. C. W., Lau, O. W., Ladd, M. F. C. & Povey, D. C. (1978). *Acta Cryst.* B**34**, 1290–1294.

Mak, T. C. W., Mok, F.-C. & Tse, J. S. (1977). *GHMC*. Quantum Chemistry Program Exchange, Indiana Univ., Bloomington, Indiana.

Mak, T. C. W., Tse, C.-S., Chong, Y.-H. & Mok, F.-C. (1977). *Acta Cryst.* B**33**, 2980–2982.

Mak, T. C. W., Yu, W.-H. & Lam, Y.-S. (1978). *Acta Cryst.* B**34**, 2061–2063.

Motherwell, W. D. S. (1976). *PLUTO*. A program for plotting molecular and crystal structures; personal communication.

Steudel, R., Reinhardt, R. & Sandow, T. (1977). *Angew. Chem. Int. Ed. Engl.* **16**, 716.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Truter, M. R. (1967). *Acta Cryst.* **22**, 556–559.