

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 ISHIDA, T., TANABE, N. & INOUE, M. (1983). *Acta Cryst.* **C39**, 110–112.  
 IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
*The Universal Crystallographic Computing System* (1979). The Computation Center, Osaka Univ.

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## A Dihydrothiocyanate Salt of a 14-Membered Tetraaza Macrocycle

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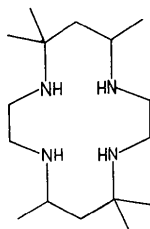
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**Abstract.**  $C_{16}H_{38}N_4^{2+} \cdot 2SCN^-$ ,  $M_r = 402.68$ , monoclinic,  $P2_1/c$ ,  $a = 7.512$  (7),  $b = 14.430$  (9),  $c = 10.691$  (8) Å,  $\beta = 104.0$  (1)°,  $U = 1124.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.15$  (2),  $D_x = 1.16$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 2.11$  cm<sup>-1</sup>,  $F(000) = 440$ , room temperature, final  $R = 0.071$  for 1039 [ $I > 3\sigma(I)$ ] independent observed reflections. The compound may be considered as a salt between hydrogen thiocyanate and the macrocyclic base *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*L*) in the form  $[LH_2]^{2+} \cdot 2[SCN]^-$ . Two of the N atoms (symmetry-related) in *L* are protonated. The thiocyanate ion is hydrogen bonded to two different macrocycles through the N and S atoms: N...N 2.78 (1) and S...N 3.50 (2) Å. There is also intramolecular hydrogen bonding to form a six-membered ring in the chair form with N...N 2.85 (2) Å.

**Introduction.** The macrocycle *L* (below) was first prepared by Curtis (1964) in a template reaction between nickel tris(ethylenediamine) and acetone; the free base was obtained by removing the metal ion from the resulting complex. Structure of the free base in the form of the dihydrate was reported by Gluźniński, Krajewski & Urbańczyk-Lipkowska (1980), while those of the salts are not known.



**Experimental.** Long crystals of the compound isolated as by-products in the preparation of the Fe<sup>II</sup> thiocyanate complex of the macrocycle. Slow recrystallization of the metal complex from chloroform-deposited crystals, the microanalysis of which showed that it was a salt of the macrocycle with hydrogen thiocyanate in the ratio of 1:2 [ $C_{16}H_{36}N_4 \cdot 2HNCS$ : Calc. % C = 53.7, H = 9.5, N = 20.9, S = 15.9; found % C = 53.5, H = 9.8, N = 20.6, S = 15.6; melting point 510 K (decomposed)].

Density measured by flotation in  $CCl_4$ /ligroin. Crystal of approximate size  $0.2 \times 0.2 \times 0.5$  mm mounted on Stoe STADI-2 diffractometer to rotate about the *a* axis. Cell dimensions calculated from  $2\theta$  measurements of 20 reflections in 30 to 40° range. Intensity data collected *via* variable-width  $\omega$  scan, background counts 20 s, step-scan rate  $0.033^\circ$  s<sup>-1</sup>, width  $(1.5 + \sin\mu/\tan\theta)$ . Absorption and extinction corrections not applied. Standard reflections *h22* measured every 20 measurements for each layer: no significant change in intensity. 1947 reflections measured with  $2\theta_{\max} 50^\circ$ ,  $h$  0 to 6,  $k$  0 to 16 and  $l$  -12 to 12. 1548 unique reflections.  $R_{\text{int}} = 0.02$ . 1039 data with  $I > 3\sigma(I)$  used in subsequent calculations.

Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) on Amdahl V7A computer. All non-hydrogen atoms refined anisotropically. Positional and thermal parameters of H atoms bonded to N – one to N(1) and two to N(4) – allowed to refine independently. H atoms bonded to the same C refined as rigid group with common thermal parameter and fixed C–H distance of 0.95 Å. Layers were given individual scale factors. Weighting scheme  $w = 1/[\sigma^2(F) + 0.002F^2]$ .  $\sigma(F)$  taken from counting statistics. Final  $R(F) = 0.071$  ( $wR = 0.080$ ,  $S = 1.878$ ) and final shift/e.s.d.  $< 0.03$ .

In final difference map, max. and min. peaks 0.26,  $-0.34 e \text{ \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.\*

**Discussion.** Fig. 1 shows the compound with its labelling scheme; hydrogen atoms bonded to carbon are omitted for clarity. For the thiocyanate ion the bond lengths are normal and the N—C—S angle at  $177.8 (6)^\circ$  is almost linear as expected. The macrocycle  $[LH_2]^{2+}$  has crystallographically imposed  $\bar{1}$  symmetry and so the four N atoms in the macrocycle are coplanar. The two symmetry-related N(4) atoms are protonated. Bond distances and angles in the macrocycle are within the range reported for such molecules. The thiocyanate ion is hydrogen-bonded to two macrocycles: the N atom is bonded to the H on N(4) out of the plane of the

macrocycle while the S atom is weakly bonded to the H on N(1<sup>ii</sup>) of another macrocycle [symmetry element (ii):  $1-x, 0.5+y, 0.5-z$ ] which is on the other side of the macrocyclic plane. Dimensions of these bonds are  $HN(42) \cdots N(13)$  2.03 (8),  $N(4) \cdots N(13)$  2.78 (7) Å,  $N(4) \cdots HN(42) \cdots N(13)$  160 (8)°,  $HN(11^{ii}) \cdots S(11)$  2.76,  $N(1^{ii}) \cdots S(11)$  3.50 (8) Å,  $N(1^{ii}) \cdots HN(11^{ii}) \cdots S(11)$  173 (6)°. Intramolecular hydrogen bonding is also present since the  $HN(41) \cdots N(1)$  distance is only 2.08 (6) Å; the other dimensions for this interaction are  $N(4) \cdots N(1)$  2.85 (6) Å and  $N(4) \cdots HN(41) \cdots N(1)$  138 (4)°. Hydrogen bonding is more clearly shown in Fig. 1 for the molecule and in Fig. 2 in the cell.

Four of the six methyl groups are in equatorial positions as shown in Fig. 1, while the other two are in axial positions. Search of the Cambridge Structural Database (1986) files shows that the structures of only seven other metal-free 1,4,8,11-tetraazacyclotetradecane compounds are known. Of these only three are centrosymmetric. The torsion angles of these three and those of the title compound are listed in Table 3.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43467 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with estimated standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j U_{ij}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
S(11)	2584 (3)	7383 (1)	4687 (2)	104 (2)
C(12)	2796 (8)	6717 (5)	3527 (8)	98 (8)
N(13)	2907 (8)	6223 (6)	2712 (7)	129 (9)
N(1)	3522 (6)	3868 (4)	-133 (4)	61 (5)
C(2)	3050 (9)	3914 (5)	1077 (5)	76 (7)
C(3)	4734 (10)	4115 (4)	2141 (5)	82 (8)
N(4)	5421 (7)	5041 (4)	2007 (5)	65 (5)
C(5)	7299 (7)	5319 (4)	2826 (5)	64 (6)
C(6)	7641 (7)	6295 (4)	2471 (5)	56 (6)
C(7)	8020 (7)	6472 (4)	1177 (5)	61 (6)
C(8)	7240 (10)	5270 (5)	4212 (5)	77 (7)
C(9)	8730 (9)	4650 (5)	2562 (7)	91 (8)
C(10)	8435 (10)	7477 (5)	1061 (7)	79 (7)

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

S(11)—C(12)	1.607 (9)	N(4)—C(5)	1.523 (7)
C(12)—N(13)	1.145 (9)	C(5)—C(6)	1.497 (8)
N(1 <sup>i</sup> )—C(7)	1.488 (5)	C(5)—C(8)	1.495 (7)
N(1)—C(2)	1.424 (7)	C(5)—C(9)	1.521 (8)
C(2)—C(3)	1.511 (9)	C(6)—C(7)	1.500 (7)
C(3)—N(4)	1.452 (8)	C(7)—C(10)	1.496 (8)
S(11)—C(12)—N(13)	177.8 (6)	N(4)—C(5)—C(9)	108.9 (5)
N(1)—C(2)—C(3)	110.2 (5)	C(6)—C(5)—C(9)	112.2 (5)
C(2)—C(3)—N(4)	110.8 (5)	C(8)—C(5)—C(9)	110.2 (5)
C(3)—N(4)—C(5)	119.2 (5)	C(5)—C(6)—C(7)	118.4 (5)
N(4)—C(5)—C(6)	107.1 (4)	N(1 <sup>i</sup> )—C(7)—C(6)	110.4 (4)
N(4)—C(5)—C(8)	108.2 (5)	N(1 <sup>i</sup> )—C(7)—C(10)	112.7 (4)
C(6)—C(5)—C(8)	110.3 (5)	C(6)—C(7)—C(10)	109.3 (5)

(i): Symmetry element  $1-x, 1-y, -z$ .

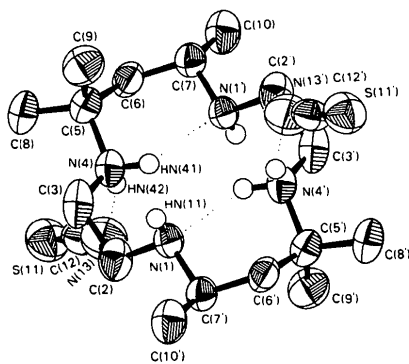


Fig. 1. The structure of  $[H_2L](NCS)_2$ , thermal ellipsoids shown at 50% probability. Hydrogen bonds shown as dotted lines.

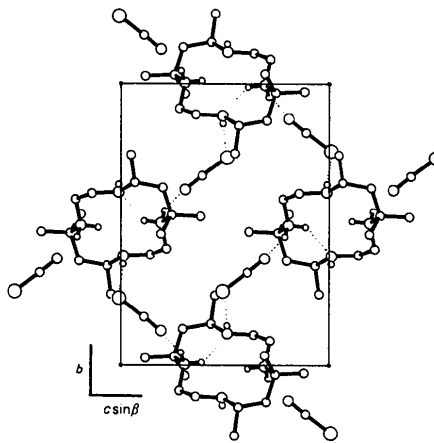


Fig. 2. The unit cell of  $[H_2L](NCS)_2$  in the *a* projection. Hydrogen bonds shown as dotted lines.

Table 3. Torsion angles ( $^{\circ}$ ) in metal-free 1,4,8,11-tetraazacyclotetradecanes

Torsion angles	(1)	(2)	(3)	(4)
N(1)–C(2)–C(3)–N(4)	67.0 (1)	66.3	63.7	49.3
C(2)–C(3)–N(4)–C(5)	–168.8 (1)	–171.3	–174.6	59.3
C(3)–N(4)–C(5)–C(6)	179.4 (1)	–176.0	–179.8	–166.7
N(4)–C(5)–C(6)–C(7)	–71.3 (1)	–72.5	–66.7	177.1
C(5)–C(6)–C(7)–N(1 <sup>1</sup> )	57.9 (1)	68.5	67.0	–59.4
C(6)–C(7)–N(1 <sup>1</sup> )–C(2 <sup>1</sup> )	–166.3 (1)	–164.2	–171.1	–74.2
C(7)–N(1 <sup>1</sup> )–C(2 <sup>1</sup> )–C(3 <sup>1</sup> )	–171.1 (1)	176.1	170.5	179.1

References: (1) this work; (2) dihydrate of 5,5,7,12,12,14-hexamethyl compound (Gluziński, Krajewski & Urbańczyk-Lipkowska, 1980); (3) diperchloric acid salt of the unsubstituted macrocycle (Nave & Truter, 1974); (4) 1,4,8,11-tetrakis(diphenylphosphino-methyl) compound (Hope, Viggiano, Moezzi & Power, 1984).

Compound (4) in Table 3 is the only one in this group with substituents at the four N atoms and the effect of substitution on the torsion angles is clearly demonstrated. The corresponding angles of the first three compounds agree to a remarkable extent, considering

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## 7,8-Dimethoxybenzo[j]fluoranthene

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**Abstract.**  $C_{22}H_{16}O_2$ ,  $M_r = 312.4$ , monoclinic,  $P2_1/c$  (No. 13),  $a = 9.488$  (3),  $b = 6.586$  (2),  $c = 25.71$  (1) Å,  $\beta = 105.09$  (2) $^{\circ}$ ,  $V = 1550.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m(\text{NaI flotation}) = 1.33$  (1),  $D_x = 1.34$  Mg m<sup>-3</sup>,  $\lambda = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.047$  mm<sup>-1</sup>,  $F(000) = 656$ ,  $T = 298$  K, final  $R = 0.042$  for 1952 observed reflections. C atoms within individual rings are coplanar within 0.1 Å but the benzo ring *E* is inclined at about 3.5 $^{\circ}$  to the plane of the naphthalenic *B* ring. In the methoxy groups, with mean dimensions C–O = 1.380 (2), O–C = 1.415 (3) Å and C–O–CH<sub>3</sub> = 114.4 (3) $^{\circ}$ , the methyl C atoms are each about 1.1 Å out of, and on opposite sides of, the molecular plane, in contrast to the planar arrangement in 5,10-dimethoxybenzo[j]fluoranthene.

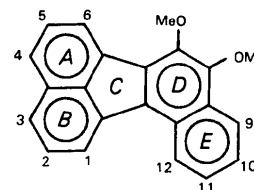
**Introduction.** Rather few structural determinations are available for methoxy-substituted non-alternant polycyclic hydrocarbons (Day, Day, Fuerniss & Wheeler, 1975; Briant, Edwards, Jones & McDonald, 1984). When a benzo ring is added to fluoranthene, which is only slightly active carcinogenically (Jones & Matthews, 1974), carcinogenic activity is appreciably

that compound (2) is not protonated at all while compound (3) is the parent macrocycle without the six methyl groups. These angles do not seem to change very much even in the case of the nickel complex (Drew & Mok, 1987).

### References

- Cambridge Structural Database (1986). Univ. Chemical Laboratory, Cambridge, England.  
 CURTIS, N. F. (1964). *J. Chem. Soc.* pp. 2644–2650.  
 DREW, M. G. B. & MOK, K. F. (1987). *Acta Cryst.* C43, 666–668.  
 GLUZIŃSKI, P., KRAJEWSKI, J. W. & URBAŃCZYK-LIPKOWSKA, Z. (1980). *Acta Cryst.* B36, 1695–1698.  
 HOPE, H., VIGGIANO, M., MOEZZI, B. & POWER, P. P. (1984). *Inorg. Chem.* 23, 2550–2552.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 NAVE, C. & TRUTER, M. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2351–2354.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

increased; the resulting compound, benzo[j]fluoranthene (B[j]F) (LaVoie, Amin, Hecht, Furuya & Hoffman, 1982), possesses a ‘pseudo *K* region’ analogous to the phenanthrenic *K* region in benz[*a*]anthracenes (Briant & Jones, 1983; Briant, Jones & Shaw, 1985). Following an X-ray and neutron study of the structure of fluoranthene (Hazell, Jones & Sowden, 1977) and an X-ray analysis of 5,10-dimethoxybenzo[j]fluoranthene (5,10-DMBF) (Briant *et al.*, 1984), we report here the structure of 7,8-dimethoxybenzo[j]fluoranthene (I) derived from B[j]F by chromate oxidation followed by reductive methylation of the 7,8-quinone.



(I)