CROATICA CHEMICA ACTA CCACAA 57 (4) 609—619 (1984)

YU ISSN 0011—1643
CCA-1474 UDC 546.492
Original Scientific Paper

A Folded Conformation of 1,4,8,11-Tetrathiacyclotetradecane in its Mercury Compound: 1,4,8,11-Tetrathiacyclotetradecanedipicratomercury(II) Heminitromethane, $[Hg(C_{10}H_{20}S_4)\cdot(C_6H_2N_3O_7)_2]\cdot 1/2CH_3NO_2$*

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Received November 17, 1983

The crystals of 1,4,8,11-tetrathiacyclotetradecanedipicratomercury(II) heminitromethane, $[Hg(C_{10}H_{20}S_4)\cdot(C_6H_2N_3O_7)_2]\cdot 1/2CH_3NO_2$, are triclinic, space group $P\bar{1}$ with $a = 1.2794(6)$, $b = 1.3108(5)$, $c = 1.0090(3)$ nm, $\alpha = 92.85(3)°$, $\beta = 107.67(3)°$, $\gamma = 94.54(4)°$, $V = 1.60236$ nm^3, and $Z = 2$. The structure was solved by the heavy atom method and refined by the least-squares method to $R = 0.030$ for the 7321 unique reflections. It consists of discrete, well separated molecules. Coordination of the mercury atom is a distorted octahedron with four sulfur atoms (Hg—S distances are 245.8(1), 251.9(1), 262..9(2), and 305.0(2) pm) from the macrocycle and two oxygen atoms (Hg—O distances are 253.1(3) and 255.8(3) pm) from the two picrates. The macrocycle is folded so that three sulfur atoms with short Hg—S bonds are in an equatorial and the fourth in an apical position. The conformation of the coordinated macrocycle is compared to the conformation of cyclotetradecane at 116 K and to the conformation of the free crystalline macrocycle.

INTRODUCTION

Thiaethers, R—S—R′, occur in numerous biologically active systems. They interact with many metal ions such as the mercuric ion which possesses a high affinity towards sulfur ligands. The coordination chemistry of mercury is interesting since mercury has numerous biological applications and is a dangerous environmental pollutant.

Crystallographic evidence of different conformations for the free 1,4,8,11-tetrathiacyclotetradecane, ([14] ane S_4), has been found by R. E. De Simone and M. D. Glick[1]. The mode of the macrocycle coordination to the metal ion

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

is dependent, among other things, on the dimensions of the ion, the macrocycle cavity and the nature of other competing ligands. When the metal ion is too large to fit into the macrocycle cavity, three possibilities exist:

— the exodentate coordination, as in the structure of $[(HgCl_2)_2([14]\text{ ane } S_4)]$[2,3];

— the planar endodentate coordination with the metal displaced out of the ring plane as in structure of $[Hg([14]\text{ ane } S_4)(H_2O)](ClO_4)_2$[3];

— the folding of the macrocycle as in the structure presented in this paper.

EXPERIMENTAL

Preparation and Crystal Data

The title compound was prepared as described previously[4]. Crystals suitable for X-ray examination were obtained by recrystallization from nitromethane.

$[C_{22}H_{24}N_6O_{14}S_4Hg] \cdot 1/2CH_3NO_2$, $M = 955.83$, triclinic, space group $P\bar{1}$ (No 2), $a = 1.2794(6)$, $b = 1.3108(5)$, $c = 1.0090(3)$ nm, $\alpha = 92.85(3)$, $\beta = 107.67(3)$, $\gamma = 94.54(4)^\circ$, $V = 1.60236$ nm^3, $Z = 2$, $D_m = 1.986$ Mgm^{-3} (by flotation in $CH_2Br_2 + CCl_4$), $D_c = 1.981$ Mgm^{-3}, μ (Mo Kα) $= 52.37$ cm^{-1}, $\lambda = 71.07$ pm, $F(000) = 940$, specimen size $0.17 \times 0.19 \times 0.32$ mm^3.

Lattice parameters were obtained from a least-squares analysis of 18 reflections with 2Θ values ranging from 11 to 18°.

*Data Collection, Structure Determination and Refinement**

9212 reflections ($2\Theta_{max} = 66^\circ$ in the range of h, k and l: from —19 to 18, ±19 and from 0 to 13, respectively) were collected on a Philips PW1100 automatic diffractometer using graphite-monochromated Mo Kα radiation ($\Theta - 2\Theta$ scan type, scan width 1.6°, scan speed 0.04° s^{-1}). 7321 reflections with $I > 5\sigma(I)$ were used for structure determination. During the data collection three standard reflections ($2\,\bar{6}\,0$, $4\,0\,2$, $0\,0\,4$) were monitored periodically; their intensities indicated no counter or crystal instability. The intensities were corrected with the ZOAK program[5] for Lorentz and polarization effects, but not for absorption.

The structure was solved by the Patterson method and completed by subsequent different Fourier syntheses and least-squares refinements. Nitromethane was not found until the final stages of the structure determination (at $R = 0.039$ with non-H atoms refined anisotropically and hydrogens isotropically). The thermal ellipsoids did not show any irregularity during the refinement, but the large empty space with six electron density maxima arround the centre of symmetry at 1/2, 1/2, 0 had a diameter of 620 pm. These maxima corresponded to one molecule of nitromethane in a disordered position with the centre of symmetry between C and N atoms. H atoms from nitromethane were not determined. The inclusion of nitromethane non-H atoms into the refinement gave $R = 0.030$ ($R_w = 0.039$, $S = 1.099$). The function minimized in the full-matrix least-squares refinement was $\Sigma w (|F_o| - |F_c|)^2$. The weighting function applied was $w = 1/\sigma^2(F_o)$, a weighting scheme of type 9 from the XRAY system[6]. The scattering factors of Cromer and Mann[7] were used for the non-H and those of Stewart et al.[8] for H atoms. Anomalous-dispersion corrections were included for Hg, S, O, N and C atoms[9]. Calculations were performed on a Univac 1110 computer at the University Computing Centre (Zagreb) with the XRAY76 system[6] and SHELX76[10]. Atomic coordinates and isotropic temperature factors are given in Table I.

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* Lists of structure factors and anisotropic thermal parameters can be obtained from the first author on request.

TABLE I

Atomic Coordinates and Isotropic Temperature Factors ($U_{eq} \times 10^{-2}$ in pm^2 for non-H atoms and $U \times 10^{-2}$ in pm^2 for H atoms) with e.s.d.'s in Parentheses

	x	*y*	*z*	
Hg	0.00065(1)	0.25842(1)	0.23706(2)	3.28(1)
		[14]aneS_4		
S1	—0.03373(9)	0.42249(8)	0.13182(12)	4.42(4)
S2	—0.20740(10)	0.31235(9)	0.30114(13)	4.95(4)
S3	—0.01157(8)	0.10541(7)	0.37509(11)	3.53(3)
S4	—0.06488(9)	0.13008(9)	0.01251(11)	4.14(4)
C1	—0.0786(5)	0.4907(3)	0.2622(6)	5.8(2)
C2	—0.1861(5)	0.4484(4)	0.2853(6)	6.0(2)
C3	—0.1276(4)	0.2974(3)	0.4812(5)	4.4(2)
C4	—0.1485(4)	0.1874(4)	0.5152(5)	4.6(2)
C5	—0.1445(4)	0.1047(3)	0.4064(5)	4.4(2)
C6	—0.0431(4)	0.0083(3)	0.2305(5)	4.2(1)
C7	—0.1257(4)	0.0299(3)	0.0936(5)	4.5(2)
C8	—0.1820(4)	0.1934(4)	—0.0884(5)	5.5(2)
C9	—0.1499(4)	0.3024(4)	—0.1160(5)	5.3(2)
C10	—0.1597(4)	0.3867(4)	—0.0123(5)	5.3(2)
H1C1	—0.033(4)	0.473(4)	0.359(5)	7(2)
H2C1	—0.080(5)	0.560(4)	0.239(6)	9(2)
H1C2	—0.176(5)	0.483(5)	0.382(6)	10(2)
H2C2	—0.254(4)	0.457(4)	0.189(6)	8(2)
H1C3	—0.053(3)	0.315(3)	0.495(4)	4(1)
H2C3	—0.149(3)	0.341(3)	0.538(4)	5(1)
H1C4	—0.095(4)	0.186(3)	0.604(5)	5(1)
H2C4	—0.220(3)	0.177(3)	0.522(4)	4(1)
H1C5	—0.160(4)	0.038(4)	0.430(5)	6(1)
H2C5	—0.200(3)	0.111(3)	0.318(4)	4(1)
H1C6	0.033(4)	—0.001(3)	0.225(5)	5(1)
H2C6	—0.068(4)	—0.046(3)	0.265(5)	5(1)
H1C7	—0.144(3)	—0.030(3)	0.025(4)	5(1)
H2C7	—0.197(3)	0.056(3)	0.106(4)	5(1)
H1C8	—0.216(4)	0.154(4)	—0.180(5)	7(2)
H2C8	—0.225(4)	0.201(4)	—0.040(5)	6(1)
H1C9	—0.075(3)	0.307(3)	—0.125(4)	4(1)
H2C9	—0.199(4)	0.308(3)	—0.209(4)	5(1)
H1C10	—0.168(4)	0.446(4)	—0.052(5)	7(2)
H2C10	—0.219(4)	0.358(4)	0.024(5)	7(1)
		Picrate 1		
O1	0.1302(2)	0.3523(2)	0.4585(3)	4.3(1)
O3	0.1973(3)	0.5085(3)	0.3371(4)	6.8(2)
O5	0.3329(4)	0.4791(4)	0.2630(5)	9.6(2)
O7	0.6243(3)	0.3044(5)	0.5356(6)	10.6(3)
O9	0.5962(3)	0.2019(4)	0.6813(6)	10.6(3)
O11	0.2470(3)	0.1453(3)	0.7421(5)	8.4(2)
O13	0.1246(3)	0.2521(3)	0.6799(4)	7.1(2)
N1	0.2776(3)	0.4630(3)	0.3407(4)	5.2(2)
N3	0.5663(4)	0.2651(4)	0.5976(6)	7.5(2)
N5	0.2122(3)	0.2204(3)	0.6796(4)	5.2(2)
C1P1	0.2303(3)	0.3393(3)	0.4994(4)	3.6(1)
C2P1	0.3120(3)	0.3888(3)	0.4432(4)	4.1(1)
C3P1	0.4182(4)	0.3653(4)	0.4723(5)	4.4(2)
C4P1	0.4547(3)	0.2935(4)	0.5692(5)	5.1(2)
C5P1	0.3867(4)	0.2480(4)	0.6366(5)	5.1(2)
C6P1	0.2792(3)	0.2718(3)	0.6042(4)	4.1(1)
HC3P1	0.468(5)	0.399(4)	0.425(6)	10(2)
HC5P1	0.412(4)	0.208(4)	0.705(5)	6(1)

	x	*y*	*z*	
		Picrate 2		
O2	0.1877(2)	0.1980(3)	0.2457(3)	5.1(1)
O4	0.2211(3)	0.0072(3)	0.3461(5)	8.3(2)
O6	0.3871(4)	0.0387(4)	0.4795(4)	8.1(2)
O8	0.6113(3)	0.0542(4)	0.1452(5)	8.3(2)
O10	0.5761(4)	0.1680(5)	—0.0015(6)	11.2(3)
O12	0.2781(3)	0.3661(3)	—0.0453(4)	6.7(2)
O14	0.1420(3)	0.3139(4)	0.0225(6)	9.7(2)
N2	0.3148(3)	0.0467(3)	0.3711(4)	5.0(1)
N4	0.5549(4)	0.1183(4)	0.0890(6)	7.1(2)
N6	0.2361(3)	0.3089(3)	0.0210(5)	5.3(2)
C1P2	0.2666(3)	0.1805(3)	0.2033(4)	3.4(1)
C2P2	0.3409(3)	0.1054(3)	0.2651(4)	3.9(1)
C3P2	0.4342(3)	0.0868(4)	0.2319(5)	4.5(1)
C4P2	0.4589(3)	0.1398(4)	0.1299(5)	4.9(2)
C5P2	0.3942(4)	0.2119(4)	0.0622(5)	4.8(2)
C6P2	0.3009(3)	0.2311(3)	0.0977(5)	4.1(1)
HC3P2	0.479(4)	0.046(3)	0.279(5)	6(1)
HC5P2	0.412(3)	0.249(3)	—0.017(4)	5(1)
		Nitromethane (on 1/2 1/2 0)		
O1N	0.4572(10)	0.5137(13)	—0.1547(14)	16.0(8)
O2N	0.5511(11)	0.4117(9)	—0.0457(19)	14.5(8)
CN	0.4984(7)	0.5223(7)	0.0589(10)	11.1(4)

The population parameters for oxygens, O1N and O2N, having centrosymmetrically related atoms, were 0.5. Carbon and nitrogen atoms were treated as carbon, CN, with population parameter 1.0.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of the title compound consists of discrete, well separated molecules. The polyhedron around the mercury atom is a distorted octahedron with three sulfur atoms from the macrocycle situated equatorially and the fourth in an apical position. The coordination is completed with two oxygens from two picrates: one is in an equatorial and the other in an apical position trans to the shortest and the longest Hg—S bonds; see Table II and Figure 1. The equatorial Hg—S distances range from 245.8(1) to 262.9(2) pm (the average value is 253.5 pm). The apical sulfur (S2) is at a greater distance from the mercury atom (305.0(2) pm) than the equatorial sulfur atoms (S1, S3 and S4). This distance is, however, shorter than the sum of the van der Waals radii (335 pm; 150 pm for mercury[11] and 185 pm for sulfur[12]). The shorter Hg—S bonds are similar to those found previously in $[(HgCl_2)_2(C_{10}H_{20}S_4)]$, where the macrocycle is twice bidentate and the mercury coordination sphere (two sulfur and two chlorine atoms) is a distorted tetrahedron; or in $[Hg(C_{10}H_{20}S_4)(H_2O)](ClO_4)_2$, where the macrocycle is quadridentate, and the mercury is coordinated to four sulfur atoms and one water oxygen atom in a distorted tetragonal pyramidal arrangement.[3].

The mercury atom lies slightly below (3.6(2) pm) the equatorial plane defined by S1, S3 and S4 atoms from the macrocycle and by the O1 atom from one picrate group. These four atoms are not coplanar, their deviations from the mean plane show tetrahedral character: S1 and S3 are below, while S4 and O1 are 41.3 pm (mean value) above the plane, see Table 4. Deviations

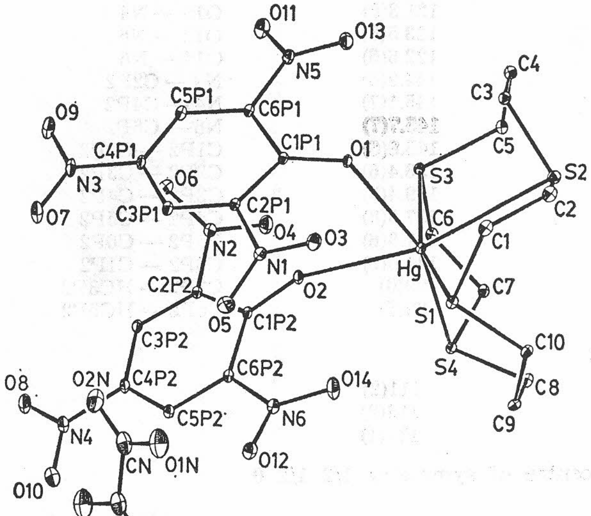

Figure 1. Perspective drawing of the molecule with atom numbering scheme.

TABLE II

Bond Distances (in pm)

a) Coordination Polyhedron Around Mercury

Hg — S1	245.8(1)	Hg — S2	305.0(2)
Hg — S3	251.9(1)	Hg — S4	262.9(2)
Hg — O1	253.1(3)	Hg — O2	255.8(3)

b) [14]aneS$_4$

S1 — C1	181.2(6)	C2 — H2C2	111(5)
S1 — C10	182.3(4)	C3 — H1C3	93(4)
S2 — C2	180.5(5)	C3 — H2C3	90(5)
S2 — C3	182.3(4)	C4 — H1C4	95(4)
S3 — C5	182.1(5)	C4 — H2C4	94(4)
S3 — C6	181.3(4)	C5 — H1C5	93(5)
S4 — C7	182.5(5)	C5 — H2C5	97(3)
S4 — C8	182.3(5)	C6 — H1C6	101(5)
C1 — C2	152.9(9)	C6 — H2C6	89(5)
C3 — C4	152.0(7)	C7 — H1C7	98(4)
C4 — C5	151.9(7)	C7 — H2C7	104(5)
C6 — C7	151.9(6)	C8 — H1C8	99(5)
C8 — C9	151.7(8)	C8 — H2C8	85(5)
C9 — C10	152.4(7)	C9 — H1C9	98(4)
C1 — H1C1	102(5)	C9 — H2C9	97(4)
C1 — H2C1	95(6)	C10 — H1C10	89(5)
C2 — H1C2	102(6)	C10 — H2C10	99(5)

c) Picrates

O1 — C1P1	124.9(5)	O2 — C1P2	124.3(6)
O3 — N1	122.1(6)	O4 — N2	121.4(6)
O5 — N1	122.0(7)	O6 — N2	121.5(5)
O7 — N3	120.8(9)	O8 — N4	120.3(7)

O9 — N3	121.3(8)	O10 — N4	123.0(9)
O11 — N5	123.5(6)	O12 — N6	122.5(6)
O13 — N5	122.6(6)	O14 — N6	121.6(6)
N1 — C2P1	144.9(6)	N2 — C2P2	145.1(7)
N3 — C4P1	145.1(7)	N4 — C4P2	145.1(7)
N5 — C6P1	145.7(7)	N6 — C6P2	146.6(6)
C1P1 — C2P1	145.8(6)	C1P2 — C2P2	145.3(6)
C2P1 — C3P1	136.4(6)	C2P2 — C3P2	137.0(7)
C3P1 — C4P1	139.4(7)	C3P2 — C4P2	136.9(7)
C4P1 — C5P1	137.5(8)	C4P2 — C5P2	137.5(7)
C5P1 — C6P1	137.8(6)	C5P2 — C6P2	138.4(7)
C6P1 — C1P1	144.0(6)	C6P2 — C1P2	144.0(7)
C3P1 — HC3P1	99(6)	C3P2 — HC3P2	86(4)
C5P1 — HC5P1	89(5)	C5P2 — HC5P2	103(5)

d) Nitromethane

O1N — CN	111(2)
O2N — CN	110(2)
CN — CN*	131(1)

* Through the centre of symmetry 1/2 1/2 0

from the equatorial plane are very similar to those found in $[Hg(C_{12}H_{24}S_4)(ClO_4)_2]$, where four sulfur atoms surround the mercury atom at an average distance of 262 pm; they are alternately displaced from their mean plane by 42 pm, while the mercury is among them, being displaced 4 pm from the mean plane[13].

The mercury-oxygen distances of 253.1(3) and 255.8(3) pm are in the same range as the four long Hg—O bonds in $HgSO_4 \cdot H_2O$ (250—251 pm)[14] and in $HgCu(OH)_2(NO_3)_2 \cdot 2H_2O$ (254—278 pm)[15] where mercury is octahedrally coordinated with two short bonds (219 and 223 pm in Ref. 14 and 230 pm in Ref. 15) and four longer ones. The angles on coordinated oxygens are quite different; Hg—O1—C1P1 is 121.5(3)° and Hg—O2—C1P2 is 157.5(3)°. Bond distances and angles in picrates are in agreement with the values obtained in other structures[16–18]. The carbon ring of the picrate *P*1 is not planar because the C1P1 atom is displaced 4.2 pm below the plane through the six carbon atoms. The substituent atoms bonded to the ring deviate still more from the best carbon plane. The carbon ring of the picrate *P*2 is nearly planar (maximum displacement is 1.1 pm) and the substituent atoms bonded to the ring deviate from the best carbon plane less than in picrate *P*1 (Table IV, Plane A).

TABLE III

Interatomic Angles in Degrees with Estimated Standard Deviations in Parentheses

a) Coordination Polyhedron Around Mercury

S1 — Hg — S2	77.05(4)	S2 — Hg — O2	165.49(8)
S1 — Hg — S3	161.93(4)	S3 — Hg — S4	87.12(4)
S1 — Hg — S4	100.51(4)	S3 — Hg — O1	88.15(8)
S1 — Hg — O1	90.33(8)	S3 — Hg — O2	83.22(9)
S1 — Hg — O2	113.94(9)	S4 — Hg — O1	158.35(8)
S2 — Hg — S3	85.10(4)	S4 — Hg — O2	81.61(8)
S2 — Hg — S4	106.39(4)	O1 — Hg — O2	76.86(10)
S2 — Hg — O1	94.22(8)		

b) [14]aneS₄

Hg — S1 — C1	100.4(2)	C2 — C1 — H1C1	92(3)
Hg — S1 — C10	101.8(2)	C2 — C1 — H2C1	113(4)

C1 — S1 — C10	104.5(2)
Hg — S2 — C2	95.8(2)
Hg — S2 — C3	84.1(2)
C2 — S2 — C3	103.4(2)
Hg — S3 — C5	105.4(1)
Hg — S3 — C6	96.9(1)
C5 — S3 — C6	101.0(2)
Hg — S4 — C7	94.9(1)
Hg — S4 — C8	98.9(2)
C7 — S4 — C8	104.4(2)
S1 — C1 — C2	117.7(3)
S1 — C1 — H1C1	109(3)
S1 — C1 — H2C1	106(4)
C3 — C4 — C5	115.7(4)
C3 — C4 — H1C4	102(3)
C3 — C4 — H2C4	109(2)
C5 — C4 — H1C4	114(3)
C5 — C4 — H2C4	104(2)
H1C4 — C4 — H2C4	111(4)
C4 — C5 — S3	114.0(3)
C4 — C5 — H1C5	113(3)
C4 — C5 — H2C5	111(2)
S3 — C5 — H1C5	106(3)
S3 — C5 — H2C5	108(3)
H1C5 — C5 — H2C5	105(3)
S3 — C6 — C7	117.6(3)
S3 — C6 — H1C6	101(2)
S3 — C6 — H2C6	102(3)
C7 — C6 — H1C6	115(3)
C7 — C6 — H2C6	111(2)
H1C6 — C6 — H2C6	109(4)
C6 — C7 — S4	109.8(3)
C6 — C7 — H1C7	112(2)
C6 — C7 — H2C7	113(2)

H1C1 — C1 — H2C1	120(4)
C1 — C2 — S2	118.2(4)
C1 — C2 — H1C2	100(3)
C1 — C2 — H2C2	107(3)
S2 — C2 — H1C2	105(3)
S2 — C2 — H2C2	101(3)
H1C2 — C2 — H2C2	126(5)
S2 — C3 — C4	109.4(3)
S2 — C3 — H1C3	110(3)
S2 — C3 — H2C3	109(2)
C4 — C3 — H1C3	111(2)
C4 — C3 — H2C3	110(3)
H1C3 — C3 — H2C3	107(4)
S4 — C7 — H1C7	105(3)
S4 — C7 — H2C7	107(2)
H1C7 — C7 — H2C7	110(3)
S4 — C8 — C9	113.0(3)
S4 — C8 — H1C8	109(3)
S4 — C8 — H2C8	109(3)
C9 — C8 — H1C8	108(3)
C9 — C8 — H2C8	103(3)
H1C8 — C8 — H2C8	115(4)
C8 — C9 — C10	116.0(5)
C8 — C9 — H1C9	109(2)
C8 — C9 — H2C9	102(2)
C10 — C9 — H1C9	111(2)
C10 — C9 —H2C9	112(3)
H1C9 — C9 — H2C9	106(4)
C9 — C10 — S1	114.2(3)
C9 — C10 — H1C10	110(3)
C9 — C10 — H2C10	104(3)
S1 — C10 — H1C10	100(3)
S1 — C10 — H2C10	110(2)
H1C10 — C10 — H2C10	119(5)

c) Picrates

Hg — O1 — C1P1	121.5(3)
O3 — N1 — O5	122.6(5)
O3 — N1 — C2P1	119.6(5)
O5 — N1 — C2P1	117.8(4)
O7 — N3 — O9	123.2(5)
O7 — N3 — C4P1	118.6(5)
O9 — N3 — C4P1	118.1(5)
O11 — N5 — O13	122.2(5)
HC3P1 — C3P1 — C2P1	120(3)
HC3P1 — C3P1 — C4P1	121(3)
C2P1 — C3P1 — C4P1	118.6(5)
N3 — C4P1 — C3P1	119.1(5)
N3 — C4P1 — C5P1	119.5(5)
C3P1 — C4P1 — C5P1	121.4(4)
HC5P1 — C5P1 — C4P1	122(3)
HC5P1 — C5P1 — C6P1	119(3)
C4P1 — C5P1 — C6P1	119.1(4)
N5 — C6P1 — C5P1	115.9(4)
N5 — C6P1 — C1P1	119.6(4)
C5P1 — C6P1 — C1P1	124.4(4)
Hg — O2 — C1P2	157.5(3)
O4 — N2 — O6	123.2(5)
O4 — N2 — C2P2	117.9(4)
O6 — N2 — C2P2	118.9(4)
O8 — N4 — O10	122.3(6)
O8 — N4 — C4P2	119.4(5)

O11 — N5 — C6P1	117.7(4)
O13 — N5 — C6P1	120.1(4)
O1 — C1P1 — C2P1	123.8(4)
O1 — C1P1 — C6P1	124.7(4)
C2P1 — C1P1 — C6P1	111.4(3)
N1 — C2P1 — C1P1	118.7(4)
N1 — C2P1 — C3P1	116.5(4)
C1P1 — C2P1 — C3P1	124.7(4)
O12 — N6 — C6P2	118.7(4)
O14 — N6 — C6P2	119.5(5)
O2 — C1P2 — C2P2	121.1(4)
O2 — C1P2 — C6P2	127.3(4)
C2P2 — C1P2 — C6P2	111.4(4)
N2 — C2P2 — C1P2	117.4(4)
N2 — C2P2 — C3P2	177.7(4)
C1P2 — C2P2 — C3P2	124.9(4)
HC3P2 — C3P2 — C2P2	121(4)
HC3P2 — C3P2 — C4P2	121(4)
C2P2 — C3P2 — C4P2	118.6(4)
N4 — C4P2 — C3P2	119.5(4)
N4 — C4P2 — C5P2	118.4(5)
C3P2 — C4P2 — C5P2	122.0(5)
HC5P2 — C5P2 — C4P2	121(3)
HC5P2 — C5P2 — C6P2	120(2)
C4P2— C5P2 — C6P2	119.0(5)
N6 — C6P2 — C5P2	115.8(4)

O10 — N4 — C4P2	118.3(5)
O12 — N6 — O14	121.7(5)
N6 — C6P2 — C1P2	120.1(4)
C5P2 — C6P2 — C1P2	124.1(4)

d) Nitromethane

O1N — CN — O2N	130(2)
O1N — CN — CN*	115(1)
O2N — CN — CN*	114(1)

TABLE IV

Mean Planes

Deviations (pm) from mean planes. E.s.d's are shown in parentheses

1. Coordination Polyhedron Around Mercury

Plane A: the plane through the four equatorial ligands
S1 —38.8(2), S3 —43.8(2), S4 38.8(2), O1 43.7(4)
distance of Hg from the plane —3.6(2)
Plane B: the plane through the three equatorial S from the macrocycle and Hg
S1 —10.9(2), S3 —10.4(2), S4 —1.6(2), Hg 23.0(2)
distance of O1 from the plane 132.5(4)
The acute angles between the carbon planes of the picrates P1 and P2 and the equatorial plane of the coordination polyhedron around mecury are 80.1(1)° and 82.6(1)°, respectively.

2. Picrates

Planes A: carbon ring P1	carbon ring P2
C1P1 —4.2(4), C2P1 3.3(4), C3P1 0.0(5) C4P1 —2.3(5), C5P1 0.9(5), C6P1 2.4(4)	C1P2 0.8(4), C2P2 —1.1(4), C3P2 0.7(5) C4P2 —0.1(5), C5P2 —0.2(5), C6P2 —0.2(5)
Distance from the plane	
O1 —18.1(3), N1 4.0(4), N3 —10.5(6), N5 5.5(4), Hg —244.6(1)	O2 8.3(4), N2 —3.5(4), N4 —3.6(6) N6 —0.4(5), Hg —15.9(1)
The acute angle between these two planes is 17.3(1)°.	
Planes B: C2P1 — C6P1	C2P2 — C6P2
C2P1 0.3(4), C3P1 0.1(5), C4P1 —0.7(5) C5P1 1.0(5), C6P1 —0.6(4)	C2P2 —0.5(4), C3P2 0.7(5), C4P2 —0.3(5) C5P2 —0.2(5), C6P2 0.3(4)
distance from the plane	
C1P1 —9.1(4), O1 —25.7(3), N1 —0.5(4) N3 —5.6(6), N5 1.0(4), Hg —254.5(1)	C1P2 1.7(4), O2 9.7(4), N2 —2.6(4), N4 —4.5(6), N6 0.4(4), Hg —13.4(1)
The acute angle between these two planes is 15.9(2)°.	
Planes C: about C1P1	about C1P2
C1P1 0.9(4), C2P1 —0.3(4), C6P1 —0.3(4), O1 —0.4(3)	C1P2 —1.6(4), C2 0.5(4), C6 0.5(4), O2 0.6(4)
distance from the plane:	
Hg —214.9(1)	Hg —34.2(1)
The acute angle between these two planes is 25.4(2)°.	
Planes D: about N1	about N2
C2P1 0.2(4), N1 —0.9(4), O3 0.3(4), O5 0.3(5)	C2P2 —0.1(4), N2 0.3(4), O4 —0.1(5), O6 —0.1(5)
Planes E: about N3	about N4
C4P1 —0.1(5), N3 0.5(6), O7 —0.2(6), O9 —0.2(6)	C4P2 0.1(5), N4 —0.4(6), O8 0.2(5), O10 0.1(6)
Planes F: about N5	about N6
C6P1 0.0(4), N5 —0.1(4), O11 0.0(5), O13 0.0(4)	C6P2 —0.2(4), N6 0.7(4), O12 —0.2(4), O14 —0.2(5)

The three nitrogroups are twisted out from the mean plane of the carbon ring P1 and P2 by 20.7(2)°, 3.5(2)°, 15.3(2)° and 47.9(2)°, 1,5(2)°, 15.8(2)°, respectively.

Bond lengths and angles in the [14] ane S_4 ring are close to the values cited for the [14] ane S_4 molecule[1], and for [14] ane S_4 in complexes with mercury[3], copper[19] and nickel[20]. The average C—S distance (181.8 pm, Table II) is in good agreement with the C—S distances in a saturated molecule[21]; the mean value of C—C distances (152.1 pm, Table II) is a bit shorter than the expected 154 pm for a single C—C bond[21]; even shorter C—C bonds of 151 pm (mean value) have been observed before in the [14] ane S_4 ring[1,20]. The average carbon-hydrogen distance is 96 pm, Table II. The C—C—C angles are close to the mean value of 115.8°; the C—S—C angles range from 101.0 to 104.5° (the mean value is 103.3°), and S—C—C from 109.4 to 118.2° (mean value is 114.2°), Table III. The Hg—S—C angles are close to each other only for S1 bonded to the mercury at the shortest distance (245.8 pm), their mean value is 101.1°. The Hg—S—C angles for S2, S3 and S4 deviate much more from each other and from the ideal tetrahedral angle; the greatest differences are for S2 connected to the mercury at the longest distance (305.0 pm), Table III.

The conformation of [14] ane S_4 in the crystals of [Hg([14] ane S_4 $(C_6H_2N_3O_7)_2] \cdot 1/2CH_3NO_2$ is not directly comparable to the conformation of the free crystalline [14] ane S_4[1]. The [14] ane S_4 in the picrate complex presents five anti conformations about S—C or C—S bonds. The free crystalline [14] ane S_4 presents six anti conformations about C—C bonds, and the conformations about C—S or S—C bonds are gauche. These conformations are comparable to the conformation of the crystalline cyclotetradecane at 116K[22], which presents two centrosymmetrically related fragments of anti, anti, gauche, gauche, anti, gauche, gauche conformations. The [14] ane S_4 in the studied complex presents no center of symmetry and has two successive anti conformations only about the bonds C7—S4 and S4—C8. We have started to compare the two rings at this point and the situation obtained is presented in Table V.

TABLE V

Dihedral Angles (°) with Standard Deviations in Parentheses

Atoms	Compound		Atoms*	Compound	
	1	2		3	4
S1—C1—C2—S2	46.3(5)	—58.0(3)	C4′—S2′—C3′—C2′	—64	—63
C1—C2—S2—C3	80.0(4)	176.0(2)	S2′—C3′—C2′—C1′	176	176
C2—S2—C3—C4	173.5(4)	—176.6(2)	C3′—C2′—C1′—S1′	—180	—179
S2—C3—C4—C5	45.8(5)	58.6(3)	C2′—C1′—S1′—C5	66	63
C3—C4—C5—S3	61.2(4)	64.4(3)	C1′—S1′—C5—C4	65	59
C4—C5—S3—C6	—174.2(3)	—170.1(2)	S1′—C5—C4—S2	175	176
C5—S3—C6—C7	64.8(4)	61.0(2)	C5—C4—S2—C3	62	69
S3—C6—C7—S4	70.9(4)	58.0(3)	C4—S2—C3—C2	64	63
C6—C7—S4—C8	—151.2(3)	—176.0(2)	S2—C3—C2—C1	—176	—176
C7—S4—C8—C9	156.6(4)	176.6(2)	C3—C2—C1—S1	180	179
S4—C8—C9—C10	—93.8(5)	—58.6(3)	C2—C1—S1—C5′	—66	—63
C8—C9—C10—S1	92.2(5)	—64.4(3)	C1—S1—C5′—C4′	—65	—59
C9—C10—S1—C1	—162.7(4)	170.1(2)	S1—C5′—C4′—S2′	—175	—176
C10—S1—C1—C2	40.6(4)	—61.0(2)	C5′—C4′—S2′—C3′	—62	—69

1. [14] ane S_4 in [Hg ([14] ane S_4) $(C_6H_2N_3O_7)_2] \cdot 1/2CH_3NO_2$
2. Cyclotetradecane at 116 K, S1, S2, S3 and S4 should read carbon, ref. 22.
3. [14] ane S_4, α form
4. [14] ane S_4, β_1 form

* The numbering of atoms is from ref. 1., α-form.

The primes represent the centrosymmetrically related atoms.

The values of dihedral angles for 3 and 4 were calculated from unit cell dimensions and coordinates given in ref. 1.

The shortest intermolecular distance of 308.8 (6) pm is between O9 and C8′ at (1 + x, y, 1 + z), Figure 2.

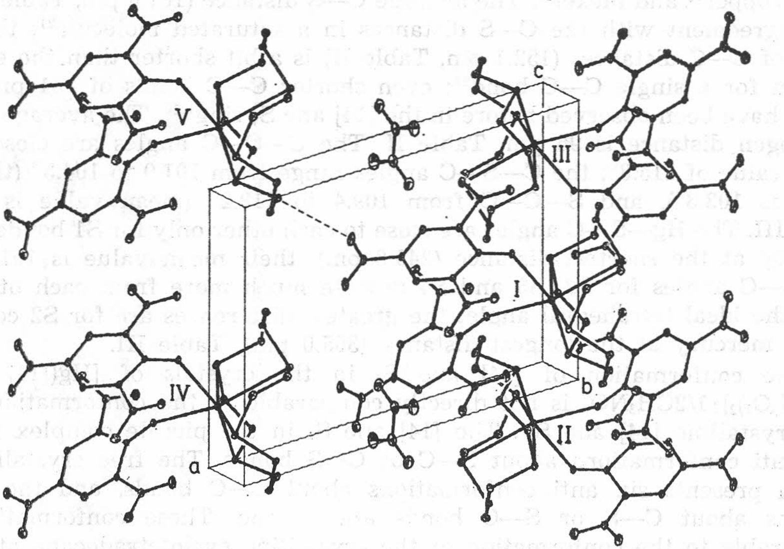

Figure 2. ORTEP drawing of the crystal structure. Dashed line indicates the shortest intermolecular distance. The presented molecules are at:

I. x, y, z;
II. $\bar{x}, \bar{y}, \bar{z}$;
III. $\bar{x}, \bar{y}, 1 - z$;
IV. $1 + x, y, z$;
V. $1 + x, y, 1 + z$.

Acknowledgement. — We thank Mr. M. Bruvo, M. Sc., for collecting the diffractometer data and the Foundation for Scientific Research of SR Croatia for financial support.

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SAŽETAK

Svinuta konformacija 1,4,8,11-tetratiociklotetradekana u živinu spoju: 1,4,8,11-tetratiociklotetradekandipikratoživa(II)-heminitrometan, $[Hg(C_{10}H_{20}S_4) \cdot (C_6H_2N_3O_7)_2] \cdot 1/2CH_3NO_2$

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Kristali 1,4,8,11-tetratiociklotetradekandipikratoživa(II)-heminitrometana, $[Hg(C_{10}H_{20}S_4) \cdot (C_6H_2N_3O_7)_2] \cdot 1/2CH_3NO_2$, jesu triklinski: prostorna grupa $P\bar{1}$, $a = 1.2794(6)$, $b = 1.3108(5)$, $c = 1.0090(3)$ nm, $\alpha = 92.85(3)^\circ$, $\beta = 107.67(3)^\circ$, $\gamma = 94.54(4)^\circ$, $V = 1.60236$ nm^3; $Z = 2$. Struktura je riješena metodom teškog atoma, a utočnjena metodom najmanjih kvadrata sa 7321 refleksom do $R = 0.030$. Struktura se sastoji od odijeljenih molekula; atom žive okružen je sa četiri atoma sumpora iz makrocikla i dva atoma kisika iz dva pikrata u obliku nepravilnog oktaedra. Makrocikl je svinut tako da su tri sumporova atoma, koji imaju kratke veze Hg—S (245,8(1), 251,9(1) i 262,9(2) pm) u ekvatorijalnim položajima, a četvrti (Hg—S = 305,0(2) pm) je u apikalnom položaju. Konformacija koordiniranog makrocikla uspoređena je s konformacijom ciklotetradekana pri 116 K i s konformacijom nekoordiniranoga, kristalnog makrocikla.