

μ -Chlorido-1:2 κ^2 Cl:Cl-trichlorido-2 κ^3 Cl-[tris(2-aminoethyl)amine-1 κ^4 N,N',N'',-N''']dimercury(II)

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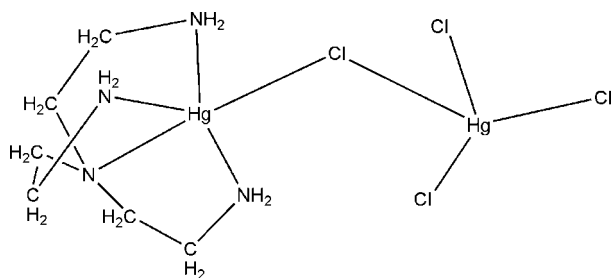
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.016$ Å; R factor = 0.038; wR factor = 0.103; data-to-parameter ratio = 19.8.

In the title complex, $[\text{Hg}_2\text{Cl}_4(\text{C}_6\text{H}_{18}\text{N}_4)]$, one Hg^{II} ion is coordinated by four N atoms from a tris(2-aminoethyl)amine ligand and one Cl atom of a tetrachloridomercurate group in a distorted trigonal-bipyramidal geometry. The Cl atom occupies an axial position and bridges to a second Hg^{II} ion, which is coordinated in a distorted tetrahedral geometry by four Cl atoms. The bonds involving the bridging Cl atom are significantly longer than the other Hg—Cl bonds. In the crystal structure, molecules are linked by intermolecular N—H \cdots Cl hydrogen bonds into a two-dimensional network, which is further stabilized by weak intermolecular C—H \cdots Cl hydrogen bonds.

Related literature

For general background, see: Adam *et al.* (1988); Gou *et al.* (1993); Cai *et al.* (1997); Wang *et al.* (1997). For related structures, see: Marchetti *et al.* (1989); Dakternicks (1990); Adam *et al.* (1994);



Experimental

Crystal data

 $[\text{Hg}_2\text{Cl}_4(\text{C}_6\text{H}_{18}\text{N}_4)]$
 $M_r = 689.22$

 Monoclinic, $P2_1/c$
 $a = 10.4378$ (6) Å

 $b = 11.5537$ (8) Å

 $c = 13.1306$ (10) Å

 $\beta = 99.395$ (1) $^\circ$
 $V = 1562.25$ (18) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 20.30$ mm⁻¹
 $T = 298$ (2) K

 $0.15 \times 0.14 \times 0.14$ mm

Data collection

 Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.151$, $T_{\text{max}} = 0.163$
 (expected range = 0.054–0.058)

 7516 measured reflections
 2757 independent reflections
 2245 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.103$
 $S = 1.07$

2757 reflections

139 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 1.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.45$ e Å⁻³
Table 1

Selected bond lengths (Å).

Hg1—N2	2.308 (8)	Hg2—Cl2	2.361 (3)
Hg1—N4	2.310 (9)	Hg2—Cl3	2.454 (3)
Hg1—N3	2.337 (8)	Hg2—Cl4	2.465 (3)
Hg1—N1	2.521 (8)	Hg2—Cl1	2.785 (3)
Hg1—Cl1	2.542 (2)		

Table 2

 Hydrogen-bond geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3B \cdots Cl3 ⁱ	0.90	2.51	3.378 (9)	163
N2—H2B \cdots Cl2 ⁱⁱ	0.90	2.78	3.590 (9)	150
N2—H2A \cdots Cl4 ^j	0.90	2.58	3.438 (9)	160
C5—H5B \cdots Cl1 ⁱⁱⁱ	0.97	2.80	3.684 (12)	153

 Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x + 1, y, z$; (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2568).

References

- Adam, K. R., Arshad, S. P. H., Baldwin, D. S., Duckworth, P. A., Leong, A. J., Lindoy, L. F., Mccool, B. J., Mcpartlin, M., Taylor, B. A. & Tasker, P. A. (1994). *Inorg. Chem.* **33**, 1194–1200.
 Adam, K. R., Dancy, K. P., Leong, A. J., Lindoy, L. F., Mcpartlin, M. & Tasker, P. A. (1988). *J. Am. Chem. Soc.* **110**, 8471–8477.
 Cai, C. X., Xue, K. H., Xu, X. Y. & Luo, Q. H. (1997). *J. Appl. Electrochem.* **27**, 793–798.
 Dakternicks, D. (1990). *Coord. Chem. Rev.* **98**, 279–294.

- Gou, S. H., You, X. Y., Yu, K. B. & Lu, J. P. (1993). *Inorg. Chem.* **32**, 1883–1887.
- Marchetti, P. S., Bank, S., Gell, T. W., Kennedy, M. A. & Ellis, P. D. (1989). *J. Am. Chem. Soc.* **111**, 2063–2066.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wang, J., Xu, X. Y., Chen, J. L., Luo, Q. H., Shen, M. C., Huang, X. Y. & Wu, Q. J. (1997). *Inorg. Chim. Acta*, **256**, 121–124.

supplementary materials

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μ -Chlorido-1:2 κ^2 Cl:Cl-trichlorido-2 κ^3 Cl-[tris(2-aminoethyl)amine-1 κ^4 N,N',N'',N''']dimercury(II)

D.-Q. Wang, Q. Wang and J.-M. Dou

Comment

Research of organic polyamines is currently of great interest because of their potential applications as useful organic ligands, in which the amine nitrogen atoms have strong coordination ability to transition metal ions and recognition function (Adam *et al.*, 1988; Marchetti *et al.*, 1989; Dakternicks, 1990; Adam *et al.*, 1994). Their transition metal complexes play an excellent role in catalysis and mimic studies on dismutase and chlorophyll (Gou *et al.*, 1993; Cai *et al.*, 1997; Wang *et al.*, 1997). In this paper, we report the synthesis and crystal structure of the title compound.

The molecular structure of the title bimetallic and bridged complex (C₆H₁₈N₄)Hg—Cl—HgCl₃ (I) is shown in Fig. 1. The coordination geometry around Hg1 atom can be described as distorted trigonal bipyramidal with the axial positions occupied by the N1 and Cl1 atoms (N1—Hg1—Cl1 = 172.4 (2) °). Atom Hg2 is four-coordinated in a distorted tetrahedral coordination geometry by one bridging Cl atoms and three terminal Cl atoms. The bond distances of Hg—N are in the range of 2.308 (8)–2.521 (8) Å, the bond distances of Hg—Cl are in the range of 2.361 (3)–2.785 (3) Å. Tris(2-aminoethyl)amine ligand consists of three five-membered chelate rings, the dihedral angle between the mean planes of these chelate rings range from 55.80 (0.28) to 64.12 (0.31) °.

In the crystal structure, adjacent molecules are linked by intermolecular N—H···Cl hydrogen bonds into a two-dimensional network which is further stabilized by weak intermolecular C—H···Cl hydrogen bonds (Fig. 2).

Experimental

Tris(2-aminoethyl)amine (2 mmol, 292.5 mg) in hot absolute ethanol (10 ml) was added dropwise to a absolute ethanol solution (20 ml) of mercury chloride (4 mmol, 868.8 mg). The mixture was heated under reflux with stirring for 5 h. The solution was kept at room temperature for about 20 days, after which large yellow block-shaped crystals of the title complex suitable for X-ray diffraction analysis were obtained.

Refinement

All H-atoms were positioned geometrically and refined using a riding model, with C—H 0.97 (methylene) and N—H (amino) 0.90 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

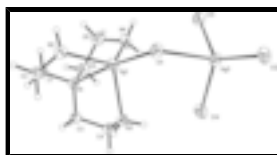


Fig. 1. The molecular structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

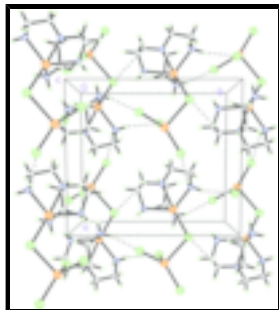


Fig. 2. Part of the crystal structure showing hydrogen bonds as dashed lines.

μ -Chlorido-1:2 κ^2 Cl-trichlorido-2 κ^3 Cl-[tris(2-aminoethyl)amine- λ 1 κ^4 N_r,Nⁱ,Nⁱⁱ,Nⁱⁱⁱ]-dimercury(II)

Crystal data

[Hg₂Cl₄(C₆H₁₈N₄)]

$M_r = 689.22$

Monoclinic, $P2_1/c$

Hall symbol: -P2ybc

$a = 10.4378$ (6) Å

$b = 11.5537$ (8) Å

$c = 13.1306$ (10) Å

$\beta = 99.3950$ (10)°

$V = 1562.25$ (18) Å³

$Z = 4$

$F_{000} = 1240$

$D_x = 2.930$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3679 reflections

$\theta = 2.4$ – 27.5 °

$\mu = 20.30$ mm⁻¹

$T = 298$ (2) K

Block, yellow

$0.15 \times 0.14 \times 0.14$ mm

Data collection

Siemens SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

$T = 298$ (2) K

ϕ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.151$, $T_{\max} = 0.163$

7516 measured reflections

2757 independent reflections

2245 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 25.0$ °

$\theta_{\min} = 2.0$ °

$h = -10 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.103$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.6626P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.07$ $(\Delta/\sigma)_{\max} = 0.001$
 2757 reflections $\Delta\rho_{\max} = 1.69 \text{ e } \text{\AA}^{-3}$
 139 parameters $\Delta\rho_{\min} = -1.45 \text{ e } \text{\AA}^{-3}$
 1 restraint Extinction correction: none
 Primary atom site location: structure-invariant direct methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.11574 (4)	0.36983 (3)	0.70931 (3)	0.03894 (16)
Hg2	-0.27774 (4)	0.42828 (4)	0.61195 (3)	0.04422 (17)
Cl1	-0.0774 (2)	0.2723 (2)	0.5996 (2)	0.04422 (17)
Cl2	-0.4650 (3)	0.3269 (3)	0.5348 (2)	0.0615 (8)
Cl3	-0.1733 (3)	0.5903 (2)	0.5366 (2)	0.0507 (7)
Cl4	-0.2391 (3)	0.4612 (3)	0.7999 (2)	0.0567 (8)
N1	0.3069 (7)	0.4444 (7)	0.8345 (6)	0.0341 (19)
N2	0.2892 (8)	0.2545 (7)	0.6860 (7)	0.042 (2)
H2A	0.2621	0.1810	0.6746	0.051*
H2B	0.3217	0.2789	0.6304	0.051*
N3	0.0576 (8)	0.3501 (8)	0.8729 (7)	0.044 (2)
H3A	-0.0271	0.3672	0.8698	0.052*
H3B	0.0701	0.2765	0.8947	0.052*
N4	0.1280 (9)	0.5653 (8)	0.6750 (8)	0.051 (2)
H4A	0.1026	0.5784	0.6072	0.061*
H4B	0.0752	0.6050	0.7101	0.061*
C1	0.4199 (10)	0.3836 (10)	0.8101 (9)	0.045 (3)
H1A	0.4875	0.3843	0.8703	0.054*
H1B	0.4524	0.4243	0.7550	0.054*
C2	0.3906 (10)	0.2588 (10)	0.7772 (8)	0.043 (3)
H2C	0.4688	0.2223	0.7616	0.052*
H2D	0.3623	0.2164	0.8333	0.052*
C3	0.2799 (9)	0.4150 (9)	0.9393 (7)	0.038 (2)
H3C	0.3298	0.4658	0.9897	0.045*
H3D	0.3071	0.3361	0.9561	0.045*
C4	0.1357 (10)	0.4275 (10)	0.9452 (8)	0.045 (3)

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H4C	0.1216	0.4101	1.0148	0.054*
H4D	0.1089	0.5068	0.9298	0.054*
C5	0.3144 (11)	0.5708 (9)	0.8183 (9)	0.047 (3)
H5A	0.4038	0.5959	0.8373	0.057*
H5B	0.2630	0.6102	0.8630	0.057*
C6	0.2654 (11)	0.6044 (10)	0.7069 (10)	0.055 (3)
H6A	0.2702	0.6877	0.6995	0.066*
H6B	0.3200	0.5692	0.6624	0.066*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0296 (3)	0.0429 (3)	0.0411 (3)	-0.00315 (17)	-0.00385 (17)	-0.00563 (17)
Hg2	0.0362 (3)	0.0502 (3)	0.0459 (3)	-0.01336 (18)	0.00534 (19)	-0.00858 (19)
Cl1	0.0362 (3)	0.0502 (3)	0.0459 (3)	-0.01336 (18)	0.00534 (19)	-0.00858 (19)
Cl2	0.0410 (16)	0.077 (2)	0.061 (2)	-0.0240 (15)	-0.0089 (13)	-0.0014 (16)
Cl3	0.0464 (16)	0.0447 (15)	0.0605 (19)	-0.0098 (13)	0.0075 (13)	0.0081 (13)
Cl4	0.0558 (18)	0.0717 (19)	0.0395 (17)	0.0081 (15)	-0.0019 (13)	-0.0160 (14)
N1	0.027 (4)	0.040 (5)	0.036 (5)	0.000 (4)	0.005 (3)	-0.007 (4)
N2	0.054 (5)	0.039 (5)	0.034 (5)	0.006 (4)	0.008 (4)	-0.010 (4)
N3	0.031 (5)	0.056 (6)	0.045 (6)	-0.007 (4)	0.009 (4)	0.003 (4)
N4	0.049 (6)	0.044 (6)	0.054 (6)	0.012 (4)	-0.005 (4)	0.006 (4)
C1	0.022 (5)	0.068 (8)	0.045 (7)	0.009 (5)	0.007 (4)	-0.006 (6)
C2	0.035 (6)	0.056 (7)	0.040 (6)	0.012 (5)	0.009 (5)	0.001 (5)
C3	0.034 (6)	0.054 (6)	0.023 (5)	0.000 (5)	0.000 (4)	-0.010 (5)
C4	0.044 (6)	0.059 (7)	0.036 (6)	0.007 (5)	0.014 (5)	-0.006 (5)
C5	0.054 (7)	0.039 (6)	0.049 (7)	-0.017 (5)	0.009 (5)	-0.010 (5)
C6	0.054 (8)	0.045 (6)	0.067 (9)	-0.001 (6)	0.015 (6)	0.008 (6)

Geometric parameters (\AA , $^\circ$)

Hg1—N2	2.308 (8)	N4—C6	1.497 (14)
Hg1—N4	2.310 (9)	N4—H4A	0.9000
Hg1—N3	2.337 (8)	N4—H4B	0.9000
Hg1—N1	2.521 (8)	C1—C2	1.521 (16)
Hg1—Cl1	2.542 (2)	C1—H1A	0.9700
Hg2—Cl2	2.361 (3)	C1—H1B	0.9700
Hg2—Cl3	2.454 (3)	C2—H2C	0.9700
Hg2—Cl4	2.465 (3)	C2—H2D	0.9700
Hg2—Cl1	2.785 (3)	C3—C4	1.526 (13)
N1—C1	1.452 (12)	C3—H3C	0.9700
N1—C5	1.480 (13)	C3—H3D	0.9700
N1—C3	1.488 (13)	C4—H4C	0.9700
N2—C2	1.463 (13)	C4—H4D	0.9700
N2—H2A	0.9000	C5—C6	1.519 (16)
N2—H2B	0.9000	C5—H5A	0.9700
N3—C4	1.453 (13)	C5—H5B	0.9700
N3—H3A	0.9000	C6—H6A	0.9700
N3—H3B	0.9000	C6—H6B	0.9700

N2—Hg1—N4	118.0 (3)	Hg1—N4—H4B	109.9
N2—Hg1—N3	113.1 (3)	H4A—N4—H4B	108.3
N4—Hg1—N3	107.8 (3)	N1—C1—C2	112.8 (8)
N2—Hg1—N1	74.3 (3)	N1—C1—H1A	109.0
N4—Hg1—N1	74.3 (3)	C2—C1—H1A	109.0
N3—Hg1—N1	74.4 (3)	N1—C1—H1B	109.0
N2—Hg1—C11	103.6 (2)	C2—C1—H1B	109.0
N4—Hg1—C11	112.8 (2)	H1A—C1—H1B	107.8
N3—Hg1—C11	100.2 (2)	N2—C2—C1	110.5 (9)
N1—Hg1—C11	172.4 (2)	N2—C2—H2C	109.6
Cl2—Hg2—Cl3	126.63 (10)	C1—C2—H2C	109.6
Cl2—Hg2—Cl4	119.67 (11)	N2—C2—H2D	109.6
Cl3—Hg2—Cl4	105.97 (11)	C1—C2—H2D	109.6
Cl2—Hg2—Cl1	103.36 (10)	H2C—C2—H2D	108.1
Cl3—Hg2—Cl1	94.75 (9)	N1—C3—C4	111.3 (8)
Cl4—Hg2—Cl1	99.00 (9)	N1—C3—H3C	109.4
Hg1—Cl1—Hg2	102.34 (9)	C4—C3—H3C	109.4
C1—N1—C5	112.5 (8)	N1—C3—H3D	109.4
C1—N1—C3	112.1 (8)	C4—C3—H3D	109.4
C5—N1—C3	112.3 (8)	H3C—C3—H3D	108.0
C1—N1—Hg1	106.0 (6)	N3—C4—C3	111.2 (8)
C5—N1—Hg1	107.4 (6)	N3—C4—H4C	109.4
C3—N1—Hg1	106.0 (5)	C3—C4—H4C	109.4
C2—N2—Hg1	110.5 (6)	N3—C4—H4D	109.4
C2—N2—H2A	109.6	C3—C4—H4D	109.4
Hg1—N2—H2A	109.6	H4C—C4—H4D	108.0
C2—N2—H2B	109.6	N1—C5—C6	111.9 (9)
Hg1—N2—H2B	109.6	N1—C5—H5A	109.2
H2A—N2—H2B	108.1	C6—C5—H5A	109.2
C4—N3—Hg1	109.8 (6)	N1—C5—H5B	109.2
C4—N3—H3A	109.7	C6—C5—H5B	109.2
Hg1—N3—H3A	109.7	H5A—C5—H5B	107.9
C4—N3—H3B	109.7	N4—C6—C5	110.4 (9)
Hg1—N3—H3B	109.7	N4—C6—H6A	109.6
H3A—N3—H3B	108.2	C5—C6—H6A	109.6
C6—N4—Hg1	108.8 (6)	N4—C6—H6B	109.6
C6—N4—H4A	109.9	C5—C6—H6B	109.6
Hg1—N4—H4A	109.9	H6A—C6—H6B	108.1
C6—N4—H4B	109.9		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3B \cdots Cl3 ⁱ	0.90	2.51	3.378 (9)	163
N2—H2B \cdots Cl2 ⁱⁱ	0.90	2.78	3.590 (9)	150
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Symmetry codes: (i) $-x, y-1/2, -z+3/2$; (ii) $x+1, y, z$; (iii) $-x, y+1/2, -z+3/2$.

Fig. 1

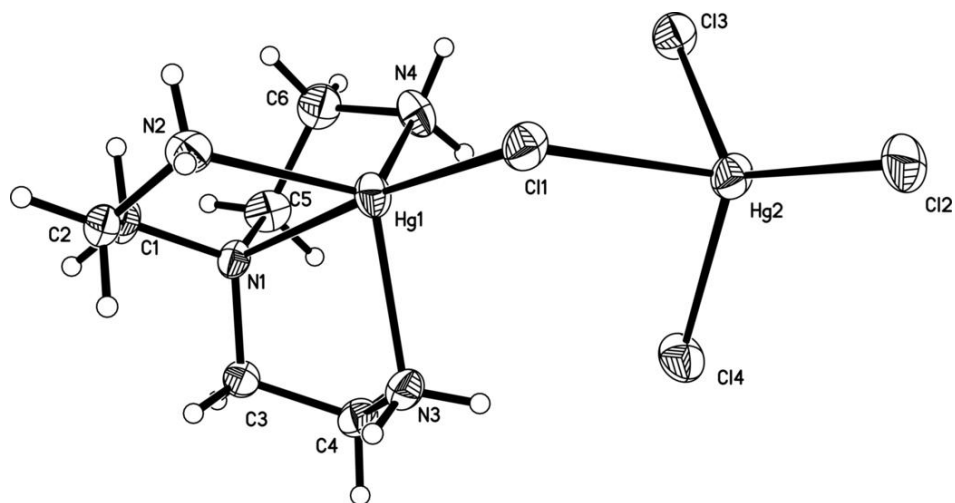


Fig. 2

