

C1—C2	1.396 (6)	C11—C12	1.423 (6)
C2—C3	1.390 (6)	C17—C18	1.508 (6)
C2—C13	1.501 (6)		
O1—Cu—N3	84.72 (13)	C12—C4—C3	118.8 (4)
O1—Cu—N2	92.78 (13)	C12—C4—C5	116.5 (4)
N3—Cu—N2	175.22 (15)	C3—C4—C5	124.7 (4)
O1—Cu—N1	165.07 (14)	C6—C5—C4	122.3 (4)
N3—Cu—N1	99.37 (14)	C5—C6—C7	121.8 (4)
N2—Cu—N1	82.05 (14)	C11—C7—C8	117.9 (4)
O1—Cu—OW1	96.51 (12)	C11—C7—C6	117.3 (4)
N3—Cu—OW1	91.28 (15)	C8—C7—C6	124.8 (4)
N2—Cu—OW1	93.05 (13)	C9—C8—C7	118.7 (4)
N1—Cu—OW1	97.74 (13)	C9—C8—C15	120.8 (4)
C1—N1—C12	117.3 (3)	C7—C8—C15	120.5 (4)
C1—N1—Cu	130.4 (3)	C8—C9—C10	118.9 (4)
C12—N1—Cu	112.3 (3)	C8—C9—C16	123.1 (4)
C10—N2—C11	117.8 (3)	C10—C9—C16	118.0 (4)
C10—N2—Cu	129.1 (3)	N2—C10—C9	123.8 (4)
C11—N2—Cu	113.1 (3)	N2—C11—C7	123.0 (4)
C18—N3—Cu	107.7 (3)	N2—C11—C12	116.1 (3)
C17—O1—Cu	115.1 (3)	C7—C11—C12	120.9 (4)
N1—C1—C2	124.6 (4)	N1—C12—C4	122.5 (4)
C3—C2—C1	118.2 (4)	N1—C12—C11	116.5 (4)
C3—C2—C13	123.1 (4)	C4—C12—C11	121.1 (4)
C1—C2—C13	118.7 (4)	O2—C17—O1	122.7 (4)
C2—C3—C4	118.7 (4)	O2—C17—C18	121.4 (4)
C2—C3—C14	120.3 (4)	O1—C17—C18	115.8 (4)
C4—C3—C14	121.0 (4)	N3—C18—C17	111.5 (3)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PC-ORTEP* (Schmid & Brueggemann, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 854–857

## Bis(tetra-*n*-butylammonium) Bis( $\mu$ -1,1-dicyanoethene-2,2-diselenolato)- dithallate(I) Acetone Solvate, [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Tl<sub>2</sub>{Se<sub>2</sub>C=C(CN)<sub>2</sub>}]<sub>2</sub>· 2(CH<sub>3</sub>)<sub>2</sub>CO

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## Abstract

In the dimeric anion two Tl atoms are coordinated by Se atoms of two different ligands forming a distorted orthorhombic bipyramid. The Bu<sub>4</sub>N<sup>+</sup> cations form hydrogen bonds with both N atoms but only one of the Se donor atoms of each ligand in the anions: C—H...N and C—H...Se distances are 2.56–2.64 (2) and 2.80–3.19 (1) Å, respectively.

## Comment

Thallium shows much greater stability as *M*<sup>I</sup> relative to *M*<sup>III</sup> than the other members of Group III in the Periodic Table. A number of thallium(I) coordination compounds with chalcogene ligands have been prepared (Lee, 1972), but only a few structural data are available. The crystal structures of various thallium(I) dialkyldithiocarbamates have been

determined (Nilson & Hesse, 1969; Jennische, Olin & Hesse, 1972; Jennische & Hesse, 1973; Anacker-Eickhoff, Jennische & Hesse, 1975; Elfwing, Anacker-Eickhoff & Jennische, 1976; Hong & Jennische, 1978). Recently, several structures of thallium(I) thiolates have been published (Krebs & Brömmelhaus, 1989, 1991). Until now however, there has been no structural information in the literature about compounds containing the selenium ligands. In this paper the crystal structure of a thallium(I) complex, (I), with the 1,1-dicyanoethene-2,2-diselenolate (*i*-mns, *iso*-maleonitrilediselenolate ligand) is described.

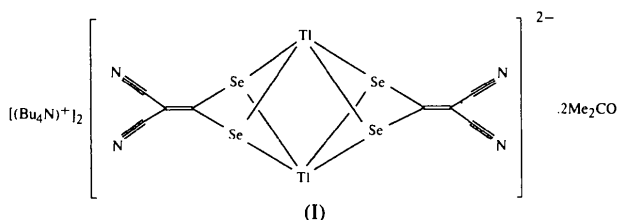


Fig. 1 shows the coordination geometry of the dimeric anion. In this centrosymmetric ion each Tl atom is linked to four Se atoms of two different *i*-mns ligands forming a slightly distorted orthorhombic bipyramid. Bond distances, bond angles and intermolecular geometry are given in Table 2. This coordination mode clearly shows the presence of the stereochemically active 6s lone pair. The common base created by the four Se atoms is planar and nearly rectangular. Comparable coordination geometry was found for Tl<sup>I</sup> dialkyldithiocarbamates (Nilson & Hesse, 1969; Jennische, Olin & Hesse, 1972; Jennische & Hesse, 1973; Anacker-Eickhoff, Jennische & Hesse, 1975; Elfwing, Anacker-Eickhoff & Jennische, 1976; Hong & Jennische, 1978), although in these the ligands have only one negative charge, thus giving neutral complexes. The Tl—Se bonds [3.132–3.207 (2) Å] are considerably shorter than those found for TlSe (3.42 Å; Man, Imanow & Semiletow, 1976) and the Tl—Tl distance [3.570 (1) Å] is comparable to those found for the dithiocarbamate complexes and is substantially longer than that found in Tl metal (3.40 Å; Pauling,

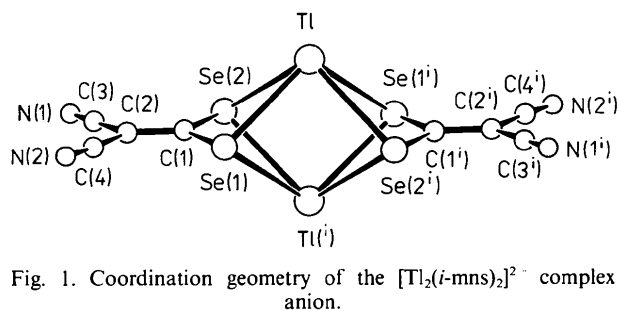


Fig. 1. Coordination geometry of the  $[\text{Tl}_2(\text{i-mns})_2]^{2-}$  complex anion.

1964). Therefore, bonding interactions between the metal centres are unlikely. Unfortunately, no further structural data for compounds with Tl—Se bonds are available in the literature. The ligand geometry agrees well with that found for related compounds (Kaiser, Dietzsch, Richter, Golić & Šiftar, 1980).

Each of the four inner C atoms connected to N(3) of the  $\text{Bu}_4\text{N}^+$  cation makes contact with the N atoms of the ligand through hydrogen bonds. Other intermolecular linkages occur through C—H...Se hydrogen bonds. Omitting the solvent molecules, Fig. 2 shows the packing of the molecules in the unit cell. Note that only one Se atom [Se(2)] of each ligand takes part in constructing the three-dimensional network, which results in a lengthening of the Se(2)—C(1) bond in comparison with the Se(1)—C(1) bond (see Table 2). The acetone molecules present in the unit cell have been found to be disordered. They are located between the vertices of the various bipyramids. The element occupying position O(1) has been identified as oxygen. O(1B) is attributed to oxygen because, of all peaks connected with molecule B, it is nearest to Tl.

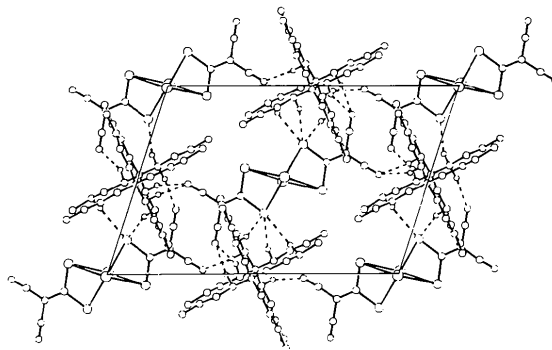


Fig. 2. Projection of the unit cell along the *b* axis. Only the H atoms involved in hydrogen bonding are shown. The disordered solvate molecules are not included.

## Experimental

The title compound was prepared by adding an aqueous solution of  $\text{TlNO}_3$  to a stirred solution of  $\text{K}_2\text{i-mns}$  [obtained by using a modification of the procedure reported by Jensen & Henriksen (1970)] and an excess of  $\text{Bu}_4\text{NBr}$  in acetonitrile and then recrystallized from acetone. The crystal was embedded in alcoholic adhesive to prevent loss of incorporated solvent acetone (proven by element analysis) during diffractometer measurements.

### Crystal data

$2(\text{C}_{16}\text{H}_{36}\text{N})[\text{Tl}_2(\text{C}_4\text{N}_2\text{Se}_2)_2] \cdot$   
 $2\text{C}_3\text{H}_6\text{O}$   
 $M_r = 1477.82$   
 Monoclinic  
 $P2_1/n$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 70  
 reflections  
 $\theta = 10.2\text{--}14.4^\circ$

$a = 12.973$  (2) Å  
 $b = 12.572$  (2) Å  
 $c = 18.993$  (2) Å  
 $\beta = 107.98$  (1)°  
 $V = 2946.4$  Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.666$  Mg m<sup>-3</sup>

$\mu = 9$  mm<sup>-1</sup>  
 $T = 296$  K  
 {011} prism and {101}  
 pinacoid  
 $0.46 \times 0.34 \times 0.34$  mm  
 Yellow

C(22B)†	0.178 (5)	0.524 (4)	0.073 (3)	0.245 (14)‡
C(23B)†	0.091 (6)	0.450 (5)	0.082 (5)	0.245 (14)‡
H5A	-0.1285 (9)	0.3670 (10)	0.5226 (6)	0.075 (16)§
H5B	0.0002 (9)	0.3566 (10)	0.5896 (6)	0.075 (16)§
H9B	0.0289 (9)	0.1171 (10)	0.5716 (7)	0.065 (16)§
H10B	0.1962 (10)	0.2784 (10)	0.5653 (7)	0.074 (17)§
H13B	-0.0506 (9)	0.3807 (9)	0.4275 (6)	0.047 (15)§
H15B	0.1456 (11)	0.4390 (13)	0.4017 (7)	0.166 (20)§
H17B	-0.0813 (10)	0.1427 (10)	0.4107 (7)	0.053 (15)§

### Data collection

Stoe Stadi 4 diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction:  
 $\psi$  scan (Flack, 1974)  
 $T_{\min} = 0.118$ ,  $T_{\max} = 0.259$

7449 measured reflections  
 6764 independent reflections  
 2263 observed reflections  
 $[I \geq 2\sigma(I)]$

### Refinement

Refinement on  $F^2$   
 $R = 0.0504$   
 $wR = 0.0474$   
 $S = 1.52$   
 2263 reflections  
 282 parameters  
 All H-atom parameters  
 refined with restraints,  
 except for those of solvent

$R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -16 \rightarrow 16$   
 $k = 0 \rightarrow 16$   
 $l = 0 \rightarrow 24$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: <2%

$w = 1/[\sigma^2(F^2) + 0.000349F^2]$   
 $(\Delta/\sigma)_{\text{max}} < 0.01$   
 $\Delta\rho_{\text{max}} = 0.73$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.59$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

† Disordered acetone molecules have been refined with geometrical restraints, isotropic displacement and constrained site occupation factors [0.621 (16) for A and 0.376 (16) for B].

‡ Due to the small scattering power of part B, a single common displacement factor was used for all atoms.

§ Refined isotropically.

Table 2. Selected geometric parameters (Å, °)

Ti—Se(1)	3.140 (2)	Ti—Se(2)	3.132 (2)
Ti—Se(1')	3.207 (2)	Ti—Se(2')	3.151 (2)
Ti...Ti'	3.570 (1)	Se(1)...Se(2)	3.207 (2)
		Se(1)...Se(2')	4.104 (2)
Se(1)—Ti—Se(2)	61.5 (1)	Se(1)—Ti'—Se(2')	80.7 (1)
Se(1)—Ti—Se(2')	60.6 (1)	Se(1)—Ti—Se(1')	111.5 (1)
Se(1)—Ti—Se(2')	81.5 (1)	Se(2)—Ti—Se(2')	110.8 (1)
Se(1)...Se(2)...Se(1')	90.9 (1)	Se(2)...Se(1)...Se(2')	89.1 (1)
Se(1)—C(1)	1.85 (1)	Se(1)—C(1)—Se(2)	117.7 (5)
Se(2)—C(1)	1.90 (1)	Se(1)—C(1)—C(2)	123.1 (7)
C(1)—C(2)	1.37 (2)	Se(2)—C(1)—C(2)	119.2 (7)
C(2)—C(3)	1.45 (2)	C(1)—C(2)—C(3)	124 (1)
C(2)—C(4)	1.44 (2)	C(1)—C(2)—C(4)	122 (1)
C(3)—N(1)	1.11 (2)	C(3)—C(2)—C(4)	114 (1)
C(4)—N(2)	1.14 (2)	C(2)—C(3)—N(1)	180 (1)
		C(2)—C(4)—N(2)	176 (1)
Se(2)...H(15B <sup>ii</sup> )	2.80 (1)	Se(2)...H(15B <sup>ii</sup> )—C(15 <sup>ii</sup> )	150 (1)
Se(2)...H(5A <sup>iii</sup> )	3.04 (1)	Se(2)...H(5A <sup>iii</sup> )—C(5 <sup>iii</sup> )	165 (1)
Se(2)...H(10B <sup>ii</sup> )	3.19 (1)	Se(2)...H(10B <sup>ii</sup> )—C(10 <sup>ii</sup> )	163 (1)
N(1)...H(13B <sup>iii</sup> )	2.58 (2)	N(1)...H(13B <sup>iii</sup> )—C(13 <sup>iii</sup> )	160 (1)
N(1)...H(5B <sup>ii</sup> )	2.64 (2)	N(1)...H(5B <sup>ii</sup> )—C(5 <sup>ii</sup> )	174 (1)
N(2)...H(17B)	2.56 (2)	N(2)...H(17B)—C(17)	170 (1)
N(2)...H(9B <sup>iv</sup> )	2.62 (2)	N(2)...H(9B <sup>iv</sup> )—C(9 <sup>iv</sup> )	158 (1)
Ti...O(1A)	3.99 (2)	Ti...O(1A)—C(22A)	125 (2)
		Ti'...Ti—O(1A)	158 (1)
Ti...O(1B <sup>v</sup> )	4.13 (5)	Ti...O(1B <sup>v</sup> )—C(22B <sup>v</sup> )	120 (3)
		Ti'...Ti—O(1B <sup>v</sup> )	135 (1)

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

The structure was solved by Patterson synthesis (SHELXS86; Sheldrick, 1985) with full-matrix least-squares refinement (SHELXL76; Sheldrick, 1976). C—H distances were restrained to 1.08 Å. Anisotropic displacement factors were refined for non-H atoms except solvent atoms; common isotropic displacement factors were used for H atoms attached to the same C atom. The SCHAKAL (Keller, 1988) program was used to prepare the figures.

AF thanks Professor Dr E. Hoyer for his interest and support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

	x	y	z	$U_{\text{eq}}$
Ti	0.01077 (5)	0.14150 (5)	-0.00132 (4)	0.0917 (3)
Se(1)	0.05863 (10)	0.00812 (15)	0.14503 (7)	0.0869 (6)
Se(2)	-0.18093 (10)	0.01855 (13)	0.02938 (7)	0.0775 (6)
N(1)	-0.3387 (9)	0.0203 (10)	0.1644 (7)	0.083 (5)
N(2)	-0.0240 (9)	0.0165 (11)	0.3234 (6)	0.085 (5)
C(1)	-0.0890 (8)	0.0152 (9)	0.1291 (6)	0.053 (4)
C(2)	-0.1344 (9)	0.0170 (10)	0.1854 (6)	0.054 (4)
C(3)	-0.2503 (12)	0.0189 (10)	0.1736 (6)	0.062 (5)
C(4)	-0.0695 (10)	0.0161 (12)	0.2618 (8)	0.072 (6)
N(3)	-0.0265 (7)	0.2488 (8)	0.4999 (6)	0.058 (4)
C(5)	-0.0674 (9)	0.3123 (10)	0.5541 (6)	0.056 (5)
C(6)	-0.1161 (10)	0.2479 (11)	0.6029 (7)	0.070 (5)
C(7)	-0.1572 (11)	0.3227 (12)	0.6498 (8)	0.089 (6)
C(8)	-0.2075 (12)	0.2651 (15)	0.7020 (9)	0.124 (8)
C(9)	0.0630 (9)	0.1716 (10)	0.5408 (7)	0.062 (5)
C(10)	0.1626 (10)	0.2203 (10)	0.5940 (7)	0.067 (6)
C(11)	0.2446 (10)	0.1356 (12)	0.6250 (9)	0.090 (6)
C(12)	0.3460 (12)	0.1753 (13)	0.6790 (10)	0.118 (8)
C(13)	0.0167 (9)	0.3311 (9)	0.4573 (6)	0.056 (5)
C(14)	0.0687 (10)	0.2902 (11)	0.4030 (7)	0.073 (6)
C(15)	0.0969 (11)	0.3833 (13)	0.3619 (7)	0.090 (6)
C(16)	0.1594 (13)	0.3484 (15)	0.3105 (9)	0.132 (8)
C(17)	-0.1160 (10)	0.1848 (10)	0.4475 (7)	0.062 (5)
C(18)	-0.2119 (10)	0.2435 (11)	0.4009 (8)	0.078 (6)
C(19)	-0.2930 (11)	0.1683 (12)	0.3536 (9)	0.094 (7)
C(20)	-0.3945 (14)	0.2188 (15)	0.3050 (11)	0.151 (9)
O(1A)†	0.1512 (5)	0.4270 (17)	0.0309 (11)	0.151 (8)
C(21A)†	0.252 (2)	0.542 (3)	0.1273 (16)	0.162 (12)
C(22A)†	0.1497 (15)	0.488 (2)	0.0805 (13)	0.110 (9)
C(23A)†	0.056 (2)	0.488 (3)	0.113 (2)	0.194 (14)
O(1B)†	0.192 (4)	0.612 (3)	0.101 (3)	0.245 (14)‡
C(21B)†	0.235 (6)	0.489 (5)	0.018 (4)	0.245 (14)‡

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## Mercury(II) Chloride Adduct of a Betaine Derivative: Bis[(dimethyl)(2-dimethylaminoethyl)ammonioacetato]tetrakis[dichloromercury(II)]

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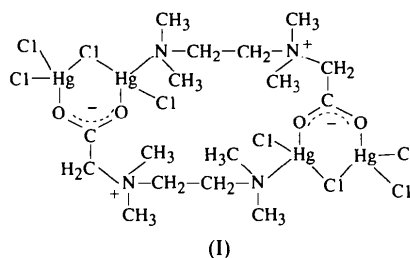
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### Abstract

The structure of a 4:2 adduct of mercury(II) chloride with a betaine derivative, di- $\mu$ -chloro-1:2 $\kappa^2$ Cl;3:4 $\kappa^2$ Cl-hexachloro-1 $\kappa^2$ Cl,2 $\kappa$ Cl,3 $\kappa^2$ Cl,4 $\kappa$ Cl-bis[ $\mu_3$ -(dimethyl)(2-dimethylaminoethyl)ammonioacetato]-1 $\kappa$ O:2 $\kappa$ O':3 $\kappa$ N';-1 $\kappa$ N':2 $\kappa$ O:3 $\kappa$ O'-tetramercury(II), [Hg<sub>4</sub>(C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>-Cl<sub>8</sub>], has been revealed as a centrosymmetric 16-membered macrocycle fused with two six-membered rings. Each of the two independent Hg<sup>II</sup> atoms is in a highly distorted tetrahedral coordination environment.

### Comment

The poor solubility of mercury(II) carboxylates in common solvents makes their structural characterization difficult. Accordingly, the crystal structures of only a few mercury(II) carboxylates and related complexes are known. Recent studies in our laboratory have demonstrated that betaine (Me<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>, IUPAC name trimethylammonioacetate, abbreviated to bet) and its derivatives, considered as neutral structural analogues of the corresponding carboxylate anions, can form soluble mercury(II) chloride adducts with the metal centre bearing additional anionic halide ligands and in different metal–betaine molar ratios (Chen & Mak, 1992). We now report the preparation and crystal structure of a mercury(II) chloride adduct of a betaine derivative, [Hg<sub>4</sub>(C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>8</sub>], namely bis[(dimethyl)(2-dimethylaminoethyl)ammonioacetato]tetrakis[dichloromercury(II)], (I).



The structure of the title complex is based on a centrosymmetric macrocycle fused with two six-membered rings (Fig. 1). Most atoms of the 16-membered macrocyclic ring [—Hg(1)—O(1)—C(1)—C(2)—N(1)—C(5)—C(6)—N(2)—Hg(1a)—O(1a)—C(1a)—C(2a)—N(1a)—C(5a)—C(6a)—N(2a)—] are nearly coplanar. Each six-membered ring adopts a twist-boat conformation with C(1)—O(1) and Hg(2)—Cl(1) as the two sides of the boat. The mean plane containing atoms Hg(1), Cl(1), Hg(2) and O(2) is nearly orthogonal to the macrocycle. The carboxylate group functions in a *syn-anti* bridge mode, which is similar to that observed in [Hg(2-ClC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>] (Mak, Yip, Kennard & Smith, 1990). The non-bonded distance of two Hg atoms bridged by the carboxylate group is 4.144 Å. The large inter-ring separations between the Hg<sup>II</sup> atoms and the nearest uncoordinated Cl atoms [Hg(1)···Cl(3b) 3.54(1) Å, Hg(2)···Cl(2c) 3.43(1) Å, Hg(2)···Cl(4d) 3.63(1) Å] indicate that the bonding interactions are negligible (see Table 3 for symmetry relationships).

The coordination geometry about each Hg<sup>II</sup> atom is distorted tetrahedral. Hg(1) is coordinated by carboxy O atom O(1), tertiary amine atom N(2a), bridging Cl atom Cl(1) and terminal Cl atom Cl(2); the four bond lengths are nearly equal [Hg(1)—O(1) 2.43(2) Å, Hg(1)—N(2a) 2.43(2) Å, Hg(1)—Cl(1) 2.435(10) Å, Hg(1)—Cl(2) 2.394(11) Å]. The bond angles range from 87.6(8) for O(1)—Hg(1)—N(2a) to