Mercury(II) Chloride Adducts of Flexible Double Betaines: Influence of Different Polymethylene Bridges Between the Quaternary Nitrogen Atoms†

De-Dong Wu and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Three mercury(II) complexes containing flexible double betaines and chloride ligands, $[\{Hg_2(L^1)Cl_4\}_n]$ **1**, $[\{Hg_4(L^2)Cl_8\}_n]$ **2** and $[\{Hg_4(L^3)Cl_8\}_n]$ **3** $[^-O_2CCH_2N^+Me_2(CH_2)_nN^+Me_2CH_2CO_2^-$; $n = 2$ L^1, 3 L^2 or 4 $L^3]$, have been prepared and shown to have similar polymeric structures by single-crystal X-ray structure analysis. In each complex the mercury atom is co-ordinated by two chloride atoms and a carboxylate oxygen atom in a distorted T-shaped fashion, and additional weak Hg···O or Hg···Cl bonds lead to six- or five-co-ordination about mercury and a two-dimensional polymeric structure. Due to the different number of methylene units between the two positively-charged quaternary nitrogen atoms in each flexible double betaine, the complexes exhibit differences in their metal–betaine molar ratios, crystal symmetries and modes of ligation of the carboxylate groups. Complexes **1** and **3** crystallize in the same monoclinic space group $P2_1/n$ with $Z = 2$, while **2** is monoclinic, space group $C2$ with $Z = 2$. With maximum separation of the two carboxymethyl groups, the flexible double betaines in **1** and **3** are each located at an inversion centre, while that in **2** lies on a C_2 axis. The carboxylate groups co-ordinate to the metal atoms in the unidentate mode in **1**, and *O*-bridging mode in **2** and **3**.

Mercury halides and carboxylates are very useful in the preparation of organic compounds *via* mercuriation.[1] The poor solubility of mercury(II) carboxylate complexes in common solvents accounts for the paucity of structural information from crystallographic studies. Simple mercury(II) carboxylates are quite rare in the literature with the majority of examples bearing additional ligands. In the typical mercury(II) carboxylate $Hg(MeCO_2)_2$,[2] the mercury atom forms two strong collinear Hg–O bonds and three weak Hg···O bonds in a square-pyramidal arrangement. The mercury atom in a mercury(II) trifluoroacetate-1,4-dioxane adduct[3] is likewise co-ordinated linearly by two ligand O atoms, but in this case four additional weak equatorial Hg···O bonds complete the resulting octahedral co-ordination. This type of co-ordination also exists in organomercury complexes such as $[HgPh(MeCO_2)]$,[4] $[C\{Hg(MeCO_2)\}_4]\cdot 2H_2O$[5] and $[C\{Hg(CF_3CO_2)\}_4]$.[6] Each mercury atom in $[Hg(2\text{-}ClC_6H_4OCH_2CO_2)_2]$[7] is bonded linearly to two carboxylate oxygen atoms, and a third ligand oxygen atom lies close to the bisector of the O–Hg–O angle to give a trigonal-planar co-ordination. Irregular five-co-ordinate arrangements have been found in $[Hg(PBu_3)(MeCO_2)_2]$,[8] $[Hg(MeS)(MeCO_2)(4Me\text{-}py)]$ and $[Hg(EtS)(MeCO_2)(4Me\text{-}py)]$ (4Me-py = 4-methylpyridine).[9] The co-ordination modes of the carboxylate groups in these examples can be classified into three types: unidentate, bidentate chelate, and bidentate bridging as discussed in the literature.[10]

We have shown that betaine ($Me_3N^+CH_2CO_2^-$, IUPAC name: trimethylammonioacetate)[11] and its derivatives, considered as neutral structural analogues of the corresponding carboxylate anions, can form soluble complexes of heavy transition metals such as Ag^I,[12] Cd^{II}[13] and Hg^{II},[10] which are amenable to structural determination by single-crystal X-ray crystallography. The mercury(II) atom in $[Hg_2(Me_3NCH_2CO_2)_2Cl_4\cdot 2HgCl_2]$[10] occurs in a distorted tetrahedral co-ordination environment, which is the same as those found in a large number of mercury(II) halide adducts with different neutral molecules, such as the tertiary phosphine adducts $HgX_2(PR_3)_n$ (n = 1 or 2; X = Cl, Br or I).[14,15] Such a co-ordination geometry about mercury has been found in several new mercury chloride adducts of betaine derivatives, for example $[Hg_2\{cis\text{-}(p\text{-}Me_2NC_5H_5N)_2C_2(CO_2)_2\}_2Cl_4\cdot 6HgCl_2]$[16] and $[Hg_2\{Me_2NCH_2CH_2NMe_2CH_2CO_2\}_2Cl_4]$.[17] Irregular five-co-ordinate arrangements about mercury occur in two betaine derivatives, $[Hg_2(C_5H_5NCH_2CO_2)_2Cl_4\cdot HgCl_2]$ and $[Hg_2(C_5H_5NCH_2CH_2CO_2)_2Cl_4]$.[10] Two uncommon co-ordination modes for the carboxylate group in mercury complexes were found, including *O*-bridging in $[Hg_2(Me_3NCH_2CO_2)_2Cl_4\cdot 2HgCl_2]$ and $[Hg_2\{cis\text{-}(p\text{-}Me_2NC_5H_5N)_2C_2(CO_2)_2\}_2Cl_4\cdot 6HgCl_2]$, and chelating plus bridging in $[Hg_2(C_5H_5NCH_2CO_2)_2Cl_4\cdot HgCl_2]$.

We now report the synthesis and crystal structure analysis of mercury chloride adducts of three flexible double betaines with different numbers of methylene units bridging two quaternary nitrogen atoms, namely *N,N,N′,N′*-tetramethylethane-1,2-diammonioacetate $[^-O_2CCH_2N^+Me_2(CH_2)_2N^+Me_2CH_2CO_2^-$, $L^1]$, *N,N,N′,N′*-tetramethylpropane-1,3-diammonioacetate $[^-O_2CCH_2N^+Me_2(CH_2)_3N^+Me_2CH_2CO_2^-$, $L^2]$ and *N,N,N′,N′*-tetramethylbutane-1,4-diammonioacetate $[^-O_2CCH_2N^+Me_2(CH_2)_4N^+Me_2CH_2CO_2^-$, $L^3]$;[18] the new complexes are $[\{Hg_2(L^1)Cl_4\}_n]$ **1**, $[\{Hg_4(L^2)Cl_8\}_n]$ **2** and $[\{Hg_4(L^3)Cl_8\}_n]$ **3**.

Experimental

Materials and Measurements.—Mercury(II) chloride was obtained from BDH. The flexible double betaines were synthesized by the reaction of ethyl chloroacetate with *N,N,N′,N′*-tetramethylethane-1,2-diamine, *N,N,N′,N′*-tetramethylpropane-1,3-diamine and *N,N,N′,N′*-tetramethylbutane-1,4-diamine.[18] Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer.

Preparation of Complexes.—$[\{Hg_2(L^1)Cl_4\}_n]$ **1**. To mercury(II) chloride (529 mg, 2.00 mmol) dissolved in boiling distilled water (15 cm^3), a solution of L^1 (123 mg, 0.50 mmol) in

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

water (5 cm^3) was added under heating. After the clear solution was cooled to room temperature, the resulting white precipitate was removed by filtration. The plate-like crystalline solid of **1**, from which a specimen was selected for the crystallographic work, was obtained by slow evaporation of the filtrate in air at room temperature. IR: 3004m, 2982m, 2946m, 2362s, 2346s, 1652vs, 1616vs, 1482m, 1446m, 1398s, 1342m, 1328m, 1166vw, 1124vw, 1005w, 977w, 913m, 899m, 794w, 723w, 667m cm^{-1}.

$[\{Hg_4(L^2)Cl_8\}_n]$ **2**. A solution of mercury(II) chloride (543 mg, 2.00 mmol) in boiling distilled water (15 cm^3) and a solution of L^2 (131 mg, 0.50 mmol) in water (5 cm^3) were mixed under heating. The resulting clear solution was allowed to evaporate at room temperature for several days to yield colourless polyhedral crystals of **2**, which were collected and air-dried. IR: 3022m, 2990m, 2956m, 2364m, 2340m, 1623vs, 1482m, 1391s, 1328m, 1054w, 1019m, 941w, 899m, 723w, 660m cm^{-1}.

$[\{Hg_4(L^3)Cl_8\}_n]$ **3**. A solution of mercury(II) chloride (548 mg, 2.00 mmol) in boiling distilled water (15 cm^3) and a solution of L^3 (143 mg, 0.50 mmol) in water (5 cm^3) were mixed under heating. After the resulting colourless solution was allowed to stand for several days at room temperature, colourless plate-like crystals of **3** were deposited, which were filtered off and air-dried. IR: 3004m, 2982m, 2946m, 2361m, 2341m, 1625vs, 1476s, 1398s, 1349m, 1335m, 1142w, 1046w, 1019m, 990w, 927w, 892s, 737w, 723w, 669m, 646m cm^{-1}.

Crystal Structure Determinations.—Information concerning the crystal data and structure refinement of the three complexes is summarized in Table 1. Intensities were collected in the variable ω-scan mode[19] on a Siemens R3m/V diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) at 293 K. Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 25 selected strong reflections. Crystal stability was monitored by recording three check reflections at intervals of 100 data measurements, and no significant variation was detected. The raw data were processed with a learnt-profile procedure,[20] and empirical absorption corrections based on ψ-scan data were also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PC program package.[21] Direct methods yielded the positions of the mercury(II) and chlorine atoms, and all non-hydrogen atoms of the double-betaine ligands were derived from subsequent Fourier difference syntheses. The last refinement cycles were performed by full-matrix least squares with anisotropic thermal parameters for the mercury and chlorine atoms and isotropic thermal parameters for the non-hydrogen atoms in the betaine ligands. The hydrogen atoms of the betaine ligands were placed in calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[22] The absolute structure of complex **2** corresponding to the reported atomic coordinates was confirmed by the fact that a parameter that multiplies all $\Delta f''$ values refined towards the value of + 1.[23] Final positional parameters for the three crystal structures, along with their estimated standard deviations, are presented in Table 2 and selected bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of Structures.—$[\{Hg_2(L^1)Cl_4\}_n]$ **1**. The structure of complex **1** is shown in Fig. 1(*a*). The mercury atom is bonded to two terminal chloride atoms [Hg(1)–Cl(1) 2.328(6), Hg(1)–Cl(2) 2.343(6) Å, Cl(1)–Hg(1)–Cl(2) 154.9(2)°] and a carboxyl oxygen atom [Hg(1)–O(1) 2.45(1) Å, Cl(1)–Hg(1)–O(1) 102.7(4), Cl(2)–Hg(1)–O(1) 98.8(4)°] in a nearly planar, distorted T-shaped co-ordination geometry. This type of co-ordination is similar to that observed in $[Hg(2\text{-}ClC_4H_4OCH_2CO_2)_2]$[7] in which the mercury atom is bound to three oxygen atoms. Another three weaker Hg ··· O bonds [Hg ··· O 2.76(1)–2.89(1) Å] lead to six-co-ordination about mercury, which is

Table 1 Data collection and processing parameters

Complex	**1**	**2**	**3**
Formula	$C_{10}H_{20}N_2O_4{\cdot}2HgCl_2$	$C_{11}H_{22}N_2O_4{\cdot}4HgCl_2$	$C_{12}H_{24}N_2O_4{\cdot}4HgCl_2$
M	775.3	1332.3	1346.3
Colour, habit	Colourless, plate	Colourless, polyhedron	Colourless, plate
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2$	$P2_1/n$
a/Å	9.150(2)	18.936(4)	11.266(3)
b/Å	7.509(2)	7.717(2)	7.758(2)
c/Å	13.947(3)	10.545(2)	16.390(3)
α/°	90	90	90
β/°	101.32(3)	117.41(3)	99.99(1)
γ/°	90	90	90
U/Å^3	939.6(5)	1367.9(7)	1410.9(7)
Z	2	2	2
D_c/g cm^{-3}	2.740	3.234	3.169
F(000)	708	1180	1196
μ/mm	16.90	23.18	22.475
Crystal size/mm	0.18 × 0.20 × 0.20	0.20 × 0.30 × 0.35	0.16 × 0.28 × 0.38
Transmission factors	0.078–0.745	0.054–0.113	0.386–0.496
2θ range/°	2–50	3–48	2–48
Unique data measured	1352	1170	2208
Observed data [$F \geqslant 4\sigma(F)$], *n*	929	943	1135
No. of variables, *p*	61	89	92
R	0.050	0.064	0.059
R′	0.054	0.082	0.065
S (goodness of fit)	1.36	1.24	1.34
Residual extremes in final difference map/e Å^{-3}	+ 1.80, − 1.13	+ 3.14, − 2.03	+ 2.65, − 2.17

$R = \Sigma\Delta/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ and $S = [w\Delta^2/(n - p)]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$, $\Delta = \big||F_o| - |F_c|\big|$; $10^4\ K$ = 2, 30 and 8 for **1**, **2** and **3**, respectively.

unlike that in the mercury(II) trifluoroacetate–1,4-dioxane(1/1) adduct.[3] This type of octahedral stereochemistry can be described as a square co-ordination about mercury plus two chelated oxygen atoms approaching the mercury atom from the same side, such that the square plane is displaced from coplanarity with the mercury atom. The carboxylate groups in the double-betaine ligand act in the unidentate mode [C(1)–O(1) 1.20(3), C(1)–O(2) 1.25(2) Å, Hg(1)–O(1)–C(1) 101(1)°] that is commonly found in many mercury(II) carboxylates such as $Hg(MeCO_2)_2$.[2] The molecular backbone of the flexible double-betaine ligand is fully extended to achieve maximum separation of its two carboxylate groups, and the molecule possesses an inversion centre at the mid-point of the C(5)–C(5a) bond. The conformation adopted by the betaine ligand is very different from that in the structure of L^1 in its hydrated form, in which the carboxylate groups are proximal as required by the C_2 symmetry. A perspective view of compound **1** is shown in Fig. 1(*b*); the *O*-bridged chains along the *b* direction are cross-linked by the double-betaine skeleton to generate a honeycomb-like layer parallel to (202), the mean plane of the group of C(4), N(1), C(5), C(5a), N(1a), C(4a) atoms being almost perpendicular to the layers.

$[\{Hg_4(L^2)Cl_8\}_n]$ **2**. Unlike **1**, complex **2** comprises two crystallographically independent mercury(II) atoms bridged by one carboxylate oxygen atom of the flexible double-betaine ligand, as shown in Fig. 2(*a*). As in the case of **1**, each mercury(II) atom is nearly linearly co-ordinated by two chlorine atoms [Hg(1)–Cl(1) 2.32(1), Hg(1)–Cl(2) 2.29(1) Å, Cl(1)–Hg(1)–Cl(2) 161.8(6)°; Hg(2)–Cl(3) 2.29(1), Hg(2)–Cl(4) 2.30(2) Å, Cl(3)–Hg(2)–Cl(4) 172.0(6)°] and a carboxylate oxygen atom [Hg(1)–O(1) 2.47(3) Å, Cl(1)–Hg(1)–O(1) 90(1), Cl(2)–Hg(1)–O(1) 101(1)°; Hg(2)–O(1) 2.67(4) Å, Cl(3)–Hg(2)–O(1) 91(1), Cl(4)–Hg(2)–O(1) 95.6(8)°] in a planar T fashion. The weak Hg···Cl and Hg···O bonds extend the co-ordination number of mercury to five. However, the co-ordination environments about the mercury atoms are different: the co-ordination geometry of Hg(1) is nearly square if the two chelating oxygen atoms of the carboxylate group are regarded as occupying one corner, whereas that of Hg(2) can be described as a square pyramid. The *O*-bridging mode in complex **2** [C(1)–O(1) 1.13(6), C(1)–O(2) 1.32(6) Å, Hg(1)–O(1)–C(1) 100(3), Hg(2)–O(1)–C(1) 131(3)°] is considered uncommon in mercury(II) carboxylates, and only found in mercury betaine adducts, such as $[Hg_2(Me_3NCH_2CO_2)_2Cl_4{\cdot}2HgCl_2]$[10] and

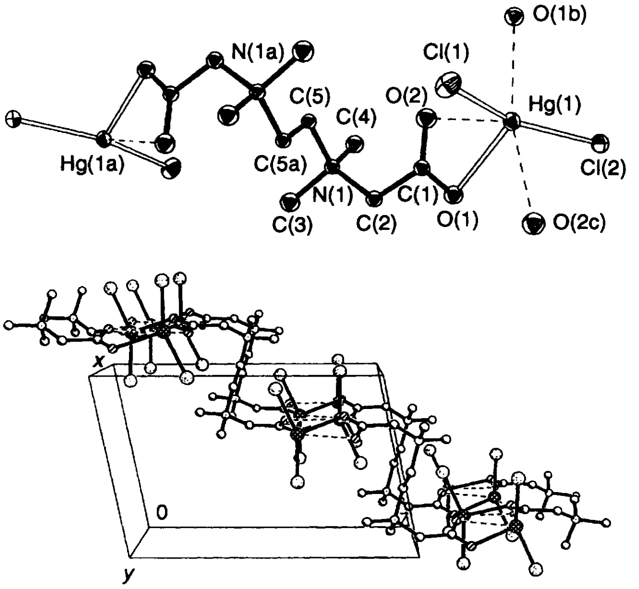

Fig. 1 (*a*) Molecular structure (35% thermal ellipsoids) of $[\{Hg_2(L^1)Cl_4\}_n]$ **1** with atom labelling. The strong and weak metal–ligand bonds are indicated by open and broken lines, respectively. (*b*) Perspective view of a layer corresponding to (202) in the crystal structure of **1**

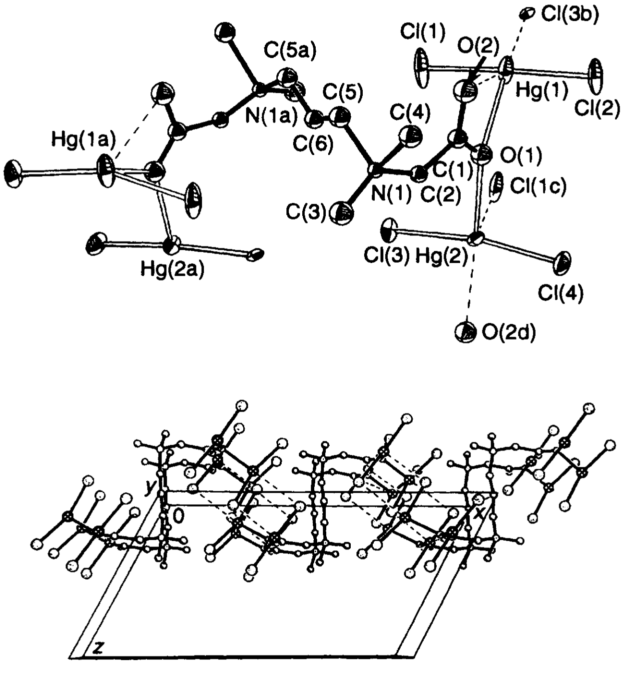

Fig. 2 (*a*) Molecular structure (35% thermal ellipsoids) of $[\{Hg_4(L^2)Cl_8\}_n]$ **2** with atom labelling. The strong and weak metal–ligand bonds are indicated by open and broken lines, respectively. (*b*) Perspective view of a layer corresponding to (001) in the crystal structure of **2**

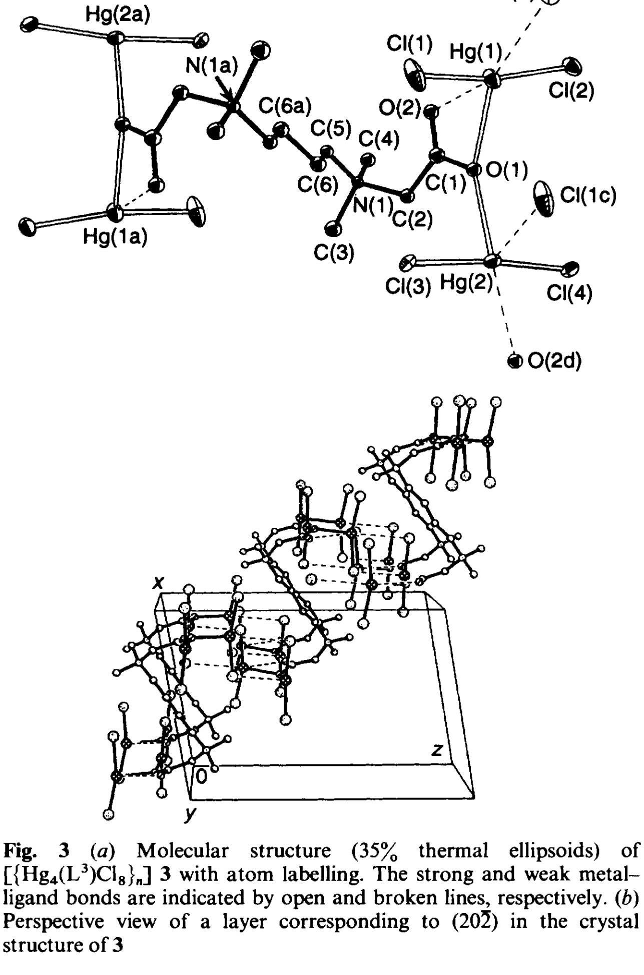

Fig. 3 (*a*) Molecular structure (35% thermal ellipsoids) of $[\{Hg_4(L^3)Cl_8\}_n]$ **3** with atom labelling. The strong and weak metal–ligand bonds are indicated by open and broken lines, respectively. (*b*) Perspective view of a layer corresponding to (20$\bar{2}$) in the crystal structure of **3**

Table 2 Atomic coordinates (× 10^4)

Atom	x	y	z
[{$Hg_2(L^1)Cl_4$}$_n$] **1**			
Hg(1)	2 371(1)	212(1)	1 779(1)
Cl(1)	−188(7)	725(9)	1 444(5)
Cl(2)	4 720(7)	−160(8)	1 375(5)
O(1)	3 161(16)	1 557(18)	3 402(10)
O(2)	2 280(17)	−1 054(20)	3 622(11)
C(1)	2 754(21)	451(25)	3 913(14)
C(2)	2 766(22)	1 073(27)	4 968(14)
N(1)	2 078(17)	−210(19)	5 640(11)
C(3)	2 023(26)	775(29)	6 550(16)
C(4)	2 946(25)	−1 809(27)	5 848(17)
C(5)	516(21)	−809(25)	5 162(14)
[{$Hg_4(L^2)Cl_8$}$_n$] **2**			
Hg(1)	7 345(1)	3 510	8 565(1)
Hg(2)	5 954(1)	8 554(9)	7 322(1)
Cl(1)	7 306(6)	3 782(54)	10 722(11)
Cl(2)	7 775(6)	3 603(41)	6 860(10)
Cl(3)	5 677(5)	8 499(28)	9 223(9)
Cl(4)	6 118(9)	8 953(16)	5 313(12)
O(1)	6 076(16)	5 100(44)	7 351(30)
O(2)	5 809(21)	2 377(60)	7 412(41)
C(1)	5 654(26)	4 050(51)	7 327(47)
C(2)	4 839(16)	4 432(42)	7 107(32)
N(1)	4 270(11)	3 750(41)	7 278(21)
C(3)	3 587(25)	4 471(61)	7 073(48)
C(4)	4 079(22)	1 909(60)	6 116(44)
C(5)	4 637(23)	2 501(61)	8 710(42)
C(6)	5 000	3 392(122)	10 000
[{$Hg_4(L^3)Cl_8$}$_n$] **3**			
Hg(1)	3 663(1)	5 106(3)	7 396(1)
Hg(2)	3 660(1)	−80(2)	5 946(1)
Cl(1)	1 570(6)	4 946(21)	7 244(4)
Cl(2)	5 677(5)	5 329(15)	7 917(4)
Cl(3)	1 612(5)	66(14)	5 557(4)
Cl(4)	5 693(7)	−457(10)	6 191(4)
O(1)	3 808(14)	3 282(23)	6 122(9)
O(2)	3 456(15)	6 053(26)	5 804(9)
C(1)	3 444(25)	4 508(38)	5 594(16)
C(2)	3 100(22)	3 923(35)	4 722(12)
N(1)	2 296(14)	5 157(32)	4 115(9)
C(3)	1 896(26)	4 105(42)	3 225(14)
C(4)	3 032(21)	6 525(35)	3 920(13)
C(5)	1 259(19)	5 798(34)	4 468(12)
C(6)	533(21)	4 609(37)	4 856(14)

Table 3 Selected bond lengths (Å) and angles (°)

[{$Hg_2(L^1)Cl_4$}$_n$] **1**			
Hg(1)–Cl(1)	2.328(6)	Hg(1)–Cl(2)	2.343(6)
Hg(1)–O(1)	2.45(1)	Hg(1) · · · O(2)	2.76(1)
Hg(1) · · · O(1b)	2.79(1)	Hg(1) · · · O(2c)	2.89(1)
O(1)–C(1)	1.20(3)	O(2)–C(1)	1.25(2)
C(1)–C(2)	1.54(3)		
Cl(1)–Hg(1)–Cl(2)	154.9(2)	Cl(1)–Hg(1)–O(1)	102.7(4)
Cl(2)–Hg(1)–O(1)	98.8(4)	Hg(1)–O(1)–C(1)	101(1)
O(1)–C(1)–O(2)	124(2)	O(1)–C(1)–C(2)	114(2)
O(2)–C(1)–C(2)	122(2)		
[{$Hg_4(L^2)Cl_8$}$_n$] **2**			
Hg(1)–Cl(1)	2.32(1)	Hg(1)–Cl(2)	2.29(1)
Hg(1)–O(1)	2.47(3)	Hg(2)–Cl(3)	2.29(1)
Hg(2)–Cl(4)	2.30(2)	Hg(2)–O(1)	2.67(4)
Hg(1) · · · O(2)	2.73(4)	Hg(1) · · · Cl(3b)	3.38(1)
Hg(2) · · · Cl(1c)	2.98(1)	Hg(2) · · · O(2d)	2.97(4)
O(1)–C(1)	1.13(6)	O(2)–C(1)	1.32(6)
C(1)–C(2)	1.48(6)		
Cl(1)–Hg(1)–Cl(2)	161.8(6)	Cl(1)–Hg(1)–O(1)	90(1)
Cl(2)–Hg(1)–O(1)	101(1)	Cl(3)–Hg(2)–Cl(4)	172.0(6)
Cl(3)–Hg(2)–O(1)	91(1)	Cl(4)–Hg(2)–O(1)	95.6(8)
Hg(1)–O(1)–C(1)	100(3)	Hg(2)–O(1)–C(1)	131(3)
Hg(1)–O(2)–C(1)	83(3)		
O(1)–C(1)–O(2)	125(5)	O(1)–C(1)–C(2)	122(4)
O(2)–C(1)–C(2)	113(4)		
[{$Hg_4(L^3)Cl_8$}$_n$] **3**			
Hg(1)–Cl(1)	2.332(7)	Hg(1)–Cl(2)	2.287(6)
Hg(1)–O(1)	2.55(2)	Hg(2)–Cl(3)	2.287(6)
Hg(2)–Cl(4)	2.275(7)	Hg(2)–O(1)	2.63(2)
Hg(1) · · · O(2)	2.681(7)	Hg(1) · · · Cl(3b)	3.422(7)
Hg(2) · · · Cl(1c)	3.021(7)	Hg(2) · · · O(2d)	3.02(2)
O(1)–C(1)	1.30(3)	O(2)–C(1)	1.25(4)
C(1)–C(2)	1.49(3)		
Cl(1)–Hg(1)–Cl(2)	164.4(2)	Cl(1)–Hg(1)–O(1)	95.2(4)
Cl(2)–Hg(1)–O(1)	98.5(4)	Cl(3)–Hg(2)–Cl(4)	172.6(3)
Cl(3)–Hg(2)–O(1)	91.3(4)	Cl(4)–Hg(2)–O(1)	93.8(4)
Hg(1)–O(1)–C(1)	95(2)	Hg(2)–O(1)–C(1)	130(2)
Hg(1)–O(2)–C(1)	90(2)		
O(1)–C(1)–O(2)	122(2)	O(1)–C(1)–C(2)	115(2)
O(2)–C(1)–C(2)	123(2)		

Symmetry codes: for **1**, (a) $-x$, $-y$, $1 - z$; (b) $0.5 - x$, $0.5 + y$, $0.5 - z$; (c) $0.5 - x$, $-0.5 + y$, $0.5 - z$; for **2**, (a) $1 - x$, y, $-z$; (b) $0.5 - x$, $0.5 + y$, $-z$; (c) $0.5 - x$, $-0.5 + y$, $-z$; (d) x, $-1 + y$, z; for **3**, (a) $-x$, $1 - y$, $1 - z$; (b) $0.5 - x$, $0.5 + y$, $1.5 - z$; (c) $0.5 - x$, $-0.5 + y$, $1.5 - z$; (d) x, $-1 + y$, z.

[Hg_2{*cis*-(p-$Me_2NC_5H_5N)_2C_2(CO_2)_2$}$_2Cl_4 \cdot 6HgCl_2$].[16] With the C(6) atom lying on a 2-axis in Wyckoff position (4*c*), the molecular backbone of the double betaine adopts a conformation that is consistent with maximum separation of its carboxylate groups. Accordingly the symmetry of the betaine ligand in this complex is higher than that of L^2 in its hydrated form.[18] The perspective view of compound **2** [Fig. 2(*b*)] shows that columns of $HgCl_2$ bridged by carboxy oxygen atoms along the *b* direction are cross-linked by the double-betaine skeleton to generate a two-dimensional polymeric network corresponding to the (001) plane, such that the mean plane of the atoms in the central portion of the double betaine [C(4), N(1), C(5), C(6), C(5a), N(1a), C(4a)] is perpendicular to the layer planes.

[{$Hg_4(L^3)Cl_8$}$_n$] **3**. The molecular backbone of the double-betaine ligand has an inversion centre at the mid-point of the C(6)–C(6a) bond. The chemical environments of the two crystallographically independent mercury atoms in complex **3** [Fig. 3(*a*)] are similar to those in **2**, despite the fact that the two complexes crystallize in different space groups. However, the intramolecular Hg(1) · · · O(2) bond [2.681(7) Å] in complex **3** is shorter whereas all the intermolecular weak Hg · · · Cl and Hg · · · O bonds are longer than the corresponding ones in complex **2**. As shown in Fig. 3(*b*), the weak bonds in the complex generate a two-dimensional network matching the (20$\bar{2}$) family of planes.

Conclusion

The present study has shown that the mercury(II) chloride adducts of a series of three flexible double betaines have polymeric structures with similar metal co-ordination but different metal–betaine molar ratios, crystal symmetries and modes of co-ordination of the carboxylate groups. The mercury(II) atoms generally prefer planar T-shaped co-ordination by chlorine atoms and an oxygen atom, which can be extended to six- or five-co-ordination by including the weak Hg · · · O and Hg · · · Cl bonds.

The different metal–ligand molar ratios and carboxylate co-ordination modes vary with the different numbers of methylene units between the two positively charged nitrogen atoms. Although the same metal–betaine molar ratio was used in the synthetic procedure, complexes with different metal–betaine molar ratios were obtained. With two methylene units in the flexible double betaine, the metal–ligand ratio is 2:1 in complex **1**. When the number increases to three and four in **2** and **3**, respectively, more space becomes available for the accommodation of additional $HgCl_2$ species, and the metal–ligand molar ratio is raised to 4:1. For the carboxylate group, the co-ordination modes vary from unidentate in **1** to *O*-bridging in **2** and **3**.

Although compounds **2** and **3** have the same metal–betaine ratio and nearly identical mercury co-ordination environments that are different from those in **1**, complexes **1** and **3** crystallize in the same monoclinic space group $P2_1/n$ with $Z = 2$, whereas complex **2** is monoclinic, space group $C2$ with $Z = 2$. Maximum separation of the two carboxymethyl groups is achieved in each of the flexible double-betaine complexes. In complexes **1** and **3**, the double-betaine ligands each have an even number of methylene units and an inversion centre, whereas in complex **2**, the odd number of bridging methylene units results in C_2 symmetry for the organic ligand.

Acknowledgements

This work is supported by a Hong Kong Research Grants Council Earmarked Grant (Ref. No. CUHK 89/93E).

References

1 J. L. Wardell, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, ch. 17, pp. 863–978.

2 R. Allmann, *Z. Kristallogr.*, 1973, **138**, 366.

3 C. H. L. Kennard and G. Smith, *Acta Crystallogr., Sect. B*, 1981, **37**, 1456.

4 B. Kamenar and M. Penavic, *Inorg. Chim. Acta*, 1972, **6**, 191.

5 D. Grdenic, B. Kamenar, B. Kamenar, B. Korpar-Colig, M. Sikirica and G. Jovanovski, *J. Chem. Soc., Chem. Commun.*, 1974, 646.

6 D. Grdenic and M. Sikirica, *Z. Kristallogr.*, 1979, **150**, 107.

7 T. C. W. Mak, W. H. Yip, C. H. L. Kennard and G. Smith, *Aust. J. Chem.*, 1990, **43**, 1431.

8 P. J. Roberts, G. Ferguson, R. G. Goel, W. O. Ogini and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1978, 253.

9 A. J. Canty, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1979, **32**, 311.

10 X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1992, 1585.

11 A. Leifer and E. R. Lippincott, *J. Am. Chem. Soc.*, 1957, **79**, 5098.

12 X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1991, 1219, 3253; *Polyhedron*, 1991, **10**, 1723, 2687.

13 X.-M. Chen and T. C. W. Mak, *J. Cryst. Spectrosc. Res.*, 1991, **21**, 27; *Aust. J. Chem.*, 1991, **44**, 639; *Acta Crystallogr., Sect. C*, 1992, **48**, 57.

14 P. A. W. Dean, *Prog. Inorg. Chem.*, 1978, **24**, 109.

15 N. A. Bell, L. A. March and I. W. Nowell, *Inorg. Chim. Acta*, 1989, **156**, 195; 1989, **162**, 57.

16 D.-D. Wu and T. C. W. Mak, *Polyhedron*, in the press.

17 D.-D. Wu and T. C. W. Mak, *Acta Crystallogr., Sect. C*, in the press.

18 D.-D. Wu and T. C. W. Mak, *J. Mol. Struct.*, 1994, **326**, 193.

19 R. Sparks, in *Crystallographic Computing Techniques*, ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976, p. 452.

20 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, 1968, **24**, 348.

21 G. M. Sheldrick, in *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, p. 506; G. M. Sheldrick, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, New York, 1985, p. 175.

22 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham (now distributed by Kluwer Academic Press, Dordrecht), 1974, vol. 4, pp. 55, 99, 149.

23 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

Received 4th July 1994; *Paper* 4/04029E