Metal–Betaine Interactions. Part 15.[1] Mercury(II) Chloride Adducts of Betaine Derivatives†

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The structures of the complexes $[\{Hg_2(Me_3NCH_2CO_2)_2Cl_4{\cdot}2HgCl_2\}_n]$ **1** $[\{Hg_2(C_5H_5NCH_2CO_2)_2Cl_4{\cdot}HgCl_2\}_n]$ **2** and $[Hg_2(C_5H_5NCH_2CH_2CO_2)_2(\mu\text{-}Cl)_2Cl_2]$ **3** have been determined by X-ray crystallography. That of **1** features a centrosymmetrical bis(carboxylato-*O*)-bridged dimeric unit with each metal atom co-ordinated by two terminal chloro ligands; the $HgCl_2$ moieties are linked by secondary bonds to the chloro ligands and oxygen atoms of neighbouring dimeric units to form a two-dimensional network. Complex **2** contains an analogous dimeric unit connected by unusual bis(carboxylato-μ-*O,O'*) bridges. Complex **3** comprises discrete dimeric molecules in which each betaine ligand functions in an unsymmetrical bidentate O,O′ mode.

Mercury(II) halides and carboxylates, especially acetate and trifluoroacetate, are very useful in the preparation of organic compounds *via* mercuriation.[2] For example, they can be used as catalysts in the synthesis of aldehydes and ketones,[3] and of stereospecific enol derivatives from alkynes.[4] The crystal structures of only a few mercury(II) carboxylates and related complexes are known. The carboxylate group commonly acts in the unidentate mode as in $[HgPh(MeCO_2)]$,[5] $[C\{Hg(F_3CCO_2)\}_4]$,[6] $[C\{Hg(MeCO_2)\}_4]{\cdot}2H_2O$,[7] and $[\{Hg\{CH[C(O)Bu^t]_2\}(MeCO_2)]$,[8] while the bidentate chelate mode is found in $[Hg(PBu_4)(MeCO_2)_2]$,[9] $[Hg(MeS)(MeCO_2)(4Me\text{-}py)]$ and $[Hg(EtS)(MeCO_2)(4Me\text{-}py)]$ (4Me-py = 4-methylpyridine).[10] Mercury(II) acetate has a one-dimensional polymeric structure with the metal atom forming two nearly linear strong Hg–O bonds (2.07 Å) and three weak secondary Hg–O bonds (2.75 Å) in a square-pyramidal arrangement,[11] while $[Hg(2\text{-}ClC_6H_4OCH_2CO_2)_2]$ also has a one-dimensional polymeric structure with the metal atom co-ordinated trigonally by a unidentate and a *syn-anti* bridging carboxylate group.[12] In the unusual charge-transfer dimeric complex $[Hg_2(F_3CCO_2)_4(C_6Me_6)_2]$ the carboxylate group functions in the *syn-syn* bridging mode.[13] On the other hand, a large number of mercury(II) halide adducts with different neutral molecules have been structurally characterized, especially tertiary phosphine adducts formulated as $HgX_2(PR_3)_n$ (n = 1 or 2; X = Cl, Br, or I). The Hg atoms are commonly in distorted-tetrahedral co-ordination, and the adducts are di- or polymeric with halide bridges for $n = 1$[14,15] and monomeric for $n = 2$.[14,16]

We have shown that betaine and its derivatives, considered as structural analogues of the corresponding carboxylate anions, can form stable soluble complexes of heavy metals such as silver(I).[1,17] The overall charge neutrality of betaines is conducive to the preparation of metal complexes in which the metal centre can bear additional anionic ligands, thus providing a ready synthetic route to mercury(II) chloride adducts. Although not structurally characterized, the 2:1 adduct of mercury(II) chloride with betaine (IUPAC name: trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$; designated as L^1) has been known since 1938.[18]

We now report the synthesis and single-crystal X-ray analysis of mercury(II) chloride adducts of betaine and two of its derivatives, namely pyridinioacetate ($C_5H_5N^+CH_2CO_2^-$, L^2) and pyridiniopropionate ($C_5H_5N^+CH_2CH_2CO_2^-$, L^3); the new complexes are $[\{Hg_2L^1_2Cl_4{\cdot}2HgCl_2\}_n]$ **1**, $[\{Hg_2L^2_2Cl_4{\cdot}HgCl_2\}_n]$ **2**, and $[Hg_2L^3_2(\mu\text{-}Cl)_2Cl_2]$ **3**.

Experimental

Preparations.—Compound L^1 was used as purchased from Sigma. The synthesis of L^3 was carried out as reported previously.[17b]

Compound L^2 was prepared by a modification of the literature method.[19] Chloroacetic acid (12.2 g, 0.10 mol) was dissolved in pyridine (100 cm^3) and the solution stirred at room temperature overnight. After removal of excess of pyridine under reduced pressure at about 60 °C a slightly yellowish crystalline powder was obtained, which was redissolved in distilled water (15 cm^3), loaded on an 'Amberlite' IRA-93 anion-exchange column (OH^- form, 4.5 × 40 cm), and eluted with distilled water (300 cm^3). The eluate was then evaporated to dryness under reduced pressure in a water-bath at *ca.* 65 °C, giving a white crystalline product (11.6 g, 85% yield), which is very hygroscopic. ^{1}H NMR (D_2O, $SiMe_4$ as internal standard): δ 5.31 (2 H, t, CH_2CO), 8.10 (2 H, t, *m*-H of py), 8.60 (1 H, t, *p*-H of py), and 8.79 (2 H, d, *o*-H of py). IR (KBr): 3292s, 3256s, 3090s, 3063s, 1634s, 1592vs, 1500m, 1489s, 1391s, 984m, 955m, 780m, 729m, 682s and 648m cm^{-1}.

$[\{Hg_2L^1_2Cl_4{\cdot}2HgCl_2\}_n]$ **1**. Mercury(II) chloride (0.272 g, 1.0 mmol) and L^1 (0.117 g, 1.0 mmol) were mixed in hot distilled water (7 cm^3). After stirring at about 90 °C for 5 min a clear solution was obtained. Slow evaporation in air at room temperature for 1 week yielded colourless polyhedral crystals. IR: 3051s, 3030s, 2966s, 1616s, 1483m, 1455m, 1398s, 1237m, 1124w, 1012w, 977m, 934m, 801m, 740m and 636m cm^{-1}.

$[\{Hg_2L^2_2Cl_4{\cdot}HgCl_2\}_n]$ **2**. Mercury(II) chloride (0.272 g, 1.0 mmol) and L^2 (0.137 g, 1.0 mmol) were added to hot distilled water (5 cm^3, 90 °C); after stirring for about 10 min the resulting clear solution was cooled to room temperature. Colourless prismatic crystals were afforded by standing overnight in air. IR: 3093s, 3065s, 3009m, 1630vs, 1505m, 1490s, 1384vs, 1307m, 1216w, 1195m, 1166w, 977w, 913w, 850m, 773m, 709s, 674s and 611vs cm^{-1}.

$[Hg_2L^3_2(\mu\text{-}Cl)_2Cl_2]$ **3**. A mixture of $HgCl_2$ (0.272 g, 1.0 mmol) and L^3 (0.151 g, 1.0 mmol) was added to water (5 cm^3) and stirred at 70 °C for 10 min, resulting in a clear solution. Colourless polyhedral crystals were afforded by slow evaporation of the solution at room temperature for several days. IR:

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Data collection and processing parameters

Complex	**1**	**2**	**3**
Formula	$C_{10}H_{22}Cl_8Hg_4N_2O_4$	$C_{14}H_{14}Cl_6Hg_3N_2O_4$	$C_{16}H_{18}Cl_4Hg_2N_2O_4$
M	1320.30	1088.77	845.34
Colour and habit	Colourless plate	Colourless polyhedron	Colourless prism
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.302(2)	7.247(5)	10.390(3)
b/Å	9.364(3)	9.093(3)	8.043(2)
c/Å	10.559(2)	9.626(5)	13.893(2)
α/°	103.48(2)	107.93(4)	90
β/°	104.45(2)	99.41(5)	108.15(2)
γ/°	97.63(2)	92.97(4)	90
U/Å^3	665.7(8)	591.8(4)	1103.0(4)
Z	1	1	2
D_c/g cm^{-3}	3.293	3.054	2.545
F(000)	564	486	776
μ/mm	23.8	20.1	14.4
Crystal size/mm	0.24 × 0.22 × 0.24	0.16 × 0.22 × 0.30	0.08 × 0.12 × 0.28
Transmission factors	0.014–0.022	0.066–0.160	0.061–0.160
Collection range, $2\theta_{max}$/°	$h, \pm k, \pm l$, 50	$h, k, \pm l$, 55	$h, k, \pm l$, 50
Unique data measured	2342	2683	1935
Observed data [$I \geqslant 3\sigma(I)$], n	1822	1603	1302
No. of variables, p	128	134	128
$R_F = \Sigma\Delta/\Sigma\lvert F_o\rvert$ [a]	0.062	0.049	0.044
$R_G = [\Sigma w\Delta^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$ [b]	0.073	0.053	0.037
$S = [\Sigma w\Delta^2/(n-p)]^{\frac{1}{2}}$	0.965	1.644	1.602
Residual extrema in final difference map (e Å^{-3})	+4.60 to −1.93	+0.67 to −1.25	+1.14 to −1.76

[a] $\Delta \equiv ||F_o| - |F_c||$. [b] Weighting scheme, $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$ where $10^4 \times K$ = 10, 4 and 1 for complexes **1**, **2** and **3**, respectively.

Table 2 Atomic coordinates (× 10^5 for Hg × 10^4 for others)

Atom	x	y	z	Atom	x	y	z
[$Hg_2L^1{}_2Cl_4$·$2HgCl_2$] **1**							
Hg(2)	94 468(11)	−36 940(8)	66 476(7)	O(2)	8 611(29)	1 165(17)	3 773(20)
Cl(3)	11 363(9)	−3 050(6)	8 838(5)	C(1)	7 794(29)	−2(18)	3 845(18)
Cl(4)	7 509(8)	−4 608(5)	4 420(5)	C(2)	8 101(38)	−1 520(19)	3 095(18)
Hg(1)	4 453(1)	−2 193(1)	5 079(1)	N(1)	7 740(22)	−1 748(15)	1 567(14)
Cl(1)	6 416(8)	−1 867(7)	7 296(5)	C(3)	9 379(48)	−878(28)	1 286(33)
Cl(2)	2 763(9)	−3 436(6)	2 795(5)	C(4)	6 033(46)	−1 198(40)	1 005(26)
O(1)	6 734(26)	−146(15)	4 556(20)	C(5)	7 524(55)	−3 379(23)	892(26)
[$Hg_2L^2{}_2Cl_4$·$HgCl_2$] **2**							
Hg(2)	50 000	50 000	50 000	C(2)	4 360(19)	335(17)	3 032(14)
Cl(3)	5 799(9)	5 893(5)	7 547(5)	N(1)	3 294(18)	−854(15)	1 637(15)
Hg(1)	6 538(10)	22 956(8)	62 707(7)	C(3)	2 516(24)	−418(20)	496(18)
Cl(1)	2 262(7)	2 243(6)	8 541(5)	C(4)	1 604(24)	−1 528(20)	−818(19)
Cl(2)	−1 483(8)	3 129(8)	4 692(6)	C(5)	1 469(25)	−3 107(20)	−942(20)
O(1)	1 538(18)	252(15)	4 000(15)	C(6)	2 267(24)	−3 542(22)	263(21)
O(2)	3 722(17)	2 190(13)	5 188(12)	C(7)	3 175(22)	−2 370(16)	1 579(20)
C(1)	3 041(22)	951(18)	4 185(18)				
[$Hg_2L^3{}_2(\mu\text{-}Cl)_2Cl_2$] **3**							
Hg(1)	17 028(6)	7 984(4)	7 811(4)	C(3)	3 022(13)	6 024(16)	3 036(9)
Cl(1)	−188(3)	−797(5)	1 227(2)	N(1)	3 010(11)	7 784(13)	3 351(8)
Cl(2)	3 569(3)	−848(6)	754(3)	C(4)	1 996(14)	8 283(19)	3 684(9)
O(1)	1 055(10)	3 311(12)	1 029(8)	C(5)	1 964(16)	9 885(19)	4 032(10)
O(2)	3 149(11)	3 196(14)	1 976(9)	C(6)	2 998(18)	10 938(20)	4 030(11)
C(1)	2 056(16)	3 946(17)	1 646(11)	C(7)	4 053(18)	10 389(21)	3 713(11)
C(2)	1 989(14)	5 693(17)	1 998(10)	C(8)	4 002(15)	8 799(18)	3 357(10)

3079m, 3058m, 1637s, 1616vs, 1574s, 1483s, 1356w, 1317w, 780m, 681s and 676m cm^{-1}.

For all three complexes the same product (checked by its IR spectrum and unit-cell dimensions) was obtained when the molar ratio of $HgCl_2$ to betaine ligand used was changed to 1:2.

Crystallography.—Diffraction intensities for each complex were collected at 21 °C on a Nicolet R3m/V diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å) and the ω-scan (2.2–14.6° min^{-1}) mode.[20] Data processing, absorption corrections, structure solution, and full-matrix least-squares refinement were performed with the SHELXTL-PLUS program package[21] (parameters listed in Table 1) on a DEC MicroVAX-II computer. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically (C–H 0.96 Å), assigned isotropic thermal factors, and included in the structure-factor calculations. Analytic expressions of neutral-atom scattering factors were employed,

Table 3 Selected interatomic distances (Å) and angles (°)

$[\{Hg_2L^1{}_2Cl_4\cdot 2HgCl_2\}_n]$ **1**			
Hg(2)–Cl(3)	2.276(5)	Hg(2)–Cl(4)	2.312(4)
Hg(1)–Cl(1)	2.346(5)	Hg(1)–Cl(2)	2.348(5)
Hg(1)–O(1)	2.62(2)	Hg(1)–O(1a)	2.45(2)
Hg(2) ··· Cl(1)	3.083(5)	Hg(2) ··· O(2b)	2.78(2)
Hg(2) ··· Cl(2c)	3.199(6)	Hg(2) ··· Cl(4d)	3.177(6)
Cl(3)–Hg(2)–Cl(4)	174.0(2)	Cl(1)–Hg(1)–Cl(2)	157.9(2)
Cl(1)–Hg(1)–O(1)	95.0(4)	Cl(2)–Hg(1)–O(1)	95.8(4)
Cl(1)–Hg(1)–O(1a)	99.1(4)	Cl(2)–Hg(1)–O(1a)	102.6(4)
O(1)–Hg(1)–O(1a)	70.8(8)	Hg(1)–O(1)–C(1)	142(1)
C(1)–O(1)–Hg(1a)	104(1)		
O(1)–C(1)	1.22(3)	O(2)–C(1)	1.20(3)
C(1)–C(2)	1.53(3)		
O(1)–C(1)–O(2)	126(2)	O(1)–C(1)–C(2)	112(2)
O(2)–C(1)–C(2)	122(2)	C(1)–C(2)–N(1)	114(2)
$[\{Hg_2L^2{}_2Cl_4\cdot HgCl_2\}_n]$ **2**			
Hg(2)–Cl(3)	2.295(5)	Hg(1)–Cl(1)	2.318(5)
Hg(1)–Cl(2)	2.311(7)	Hg(1)–O(1)	2.59(1)
Hg(1)–O(2)	2.60(1)	Hg(1)–O(1a)	2.66(1)
Hg(2) ··· O(2)	2.74(1)	Hg(2) ··· Cl(2c)	3.141(7)
Cl(1)–Hg(1)–Cl(2)	156.2(2)	Cl(1)–Hg(1)–O(1)	113.8(3)
Cl(2)–Hg(1)–O(1)	90.1(3)	Cl(1)–Hg(1)–O(2)	92.1(3)
Cl(2)–Hg(1)–O(2)	104.8(3)	O(1)–Hg(1)–O(2)	49.9(4)
Cl(1)–Hg(1)–O(1a)	90.0(3)	Cl(2)–Hg(1)–O(1a)	94.7(3)
O(1)–Hg(1)–O(1a)	77.1(5)	O(2)–Hg(1)–O(1a)	122.4(4)
Hg(1)–O(1)–C(1)	92(1)	O(1)–O(1)–Hg(1a)	152(1)
Hg(1)–O(2)–C(1)	90(1)		
O(1)–C(1)	1.19(2)	O(2)–C(1)	1.25(2)
C(1)–C(2)	1.57(2)	C(2)–N(1)	1.50(2)
O(1)–C(1)–O(2)	127(2)	O(1)–C(1)–C(2)	119(1)
O(2)–C(1)–C(2)	113(1)	C(1)–C(2)–N(1)	111(1)
$[HgL^3{}_2(\mu\text{-}Cl)_2Cl_2]$ **3**			
Hg(1)–Cl(1)	2.578(4)	Hg(1)–Cl(2)	2.358(4)
Hg(1)–O(1)	2.191(9)	Hg(1)–O(2)	2.679(9)
Hg(1)–Cl(1a)	2.743(3)		
Cl(1)–Hg(1)–Cl(2)	114.6(1)	Cl(1)–Hg(1)–O(2)	122.1(3)
Cl(1)–Hg(1)–O(1)	97.3(3)	Cl(1a)–Hg(1)–O(2)	131.6(3)
Cl(1a)–Hg(1)–Cl(2)	101.4(1)	Cl(1a)–Hg(1)–O(1)	93.0(3)
Cl(1)–Hg(1)–Cl(1a)	90.3(1)	Cl(2)–Hg(1)–O(1)	144.6(3)
Cl(2)–Hg(1)–O(2)	96.3(3)	O(1)–Hg(1)–O(2)	51.6(5)
Hg(1)–O(1)–C(1)	104.9(9)	Hg(1)–O(2)–C(2)	81.3(9)
O(1)–C(1)	1.23(2)	O(2)–C(1)	1.24(2)
C(1)–C(2)	1.50(2)	C(2)–C(3)	1.53(2)
O(1)–C(1)–O(2)	122(1)	O(1)–C(1)–C(2)	120(1)
O(2)–C(1)–C(2)	117(1)	C(1)–C(2)–C(3)	112(1)

Symmetry codes: for **1**, a 1 – *x*, –*y*, 1 – *z*; b 2 – *x*, –*y*, 1 – *z*; c 1 – *x*, –1 + *y*, 1 – *z*; d 2 – *x*, –1 + *y*, 1 – *z*; for **2**, a –*x*, –*y*, 1 – *z*; b 1 – *x*, 1 – *y*, 1 – *z*; c 1 + *x*, *y*, *z*; d –*x*, 1 – *y*, 1 – *z*; for **3**, a –*x*, –*y*, –*z*.

and anomalous dispersion corrections were incorporated.[22] The final discrepancy indices and other parameters at the conclusion of refinement are listed in Table 1, atomic coordinates are given in Table 2, and selected interatomic distances and bond 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

$[\{Hg_2L^1{}_2Cl_4\cdot 2HgCl_2\}_n]$ **1**.—Complex **1** primarily consists of centrosymmetrical bis(carboxylato)bridged $Hg_2L^1{}_2Cl_4$ dimeric units (Fig. 1) and virtually linear $HgCl_2$ units [Hg–Cl 2.276(5), 2.312(4) Å; Cl–Hg–Cl 174.0(2)°]. In the dimeric unit a pair of Hg(1) atoms, separated at a non-bonded distance of 4.129(3) Å, are bridged by two carboxylato oxygen atoms [Hg–O 2.45(2), 2.62(2) Å], and each metal atom is co-ordinated by two terminal chloro ligands [Hg–Cl 2.346(5), 2.348(5) Å] in a highly distorted tetrahedral geometry with bond angles ranging from O(1)–Hg(1)–O(1a) at 70.8(8)° to Cl(1)–Hg(1)–Cl(2) at 157.9(2)°. This significant distortion may be attributed to the fact that the chlorine atom is a stronger σ donor (hence leading to greater repulsion between the chloro ligand bond pairs at the metal centre) than a carboxylato oxygen atom, so that the two chloro ligands in **1** favour stronger bonding with Hg^{II} and a tendency toward linear co-ordination, which has been observed for mercury(II) halide adducts of phosphines.[14–16] The second oxygen atom, *i.e.* O(2) in the same carboxy group is 2.96(1) Å from the Hg(1) atom, showing clearly that the carboxylato group does not behave as a bidentate ligand.

The O-bridging mode is common in metal alkoxide chemistry,[23a] one example being the copper(I) complex $[\{Cu(OBu^t)\}_4]$,[24] where each pair of metal atoms are bridged by an oxygen atom of the alkoxide to form a tetrameric structure. In contrast, this one-atom bridge is seldom the only

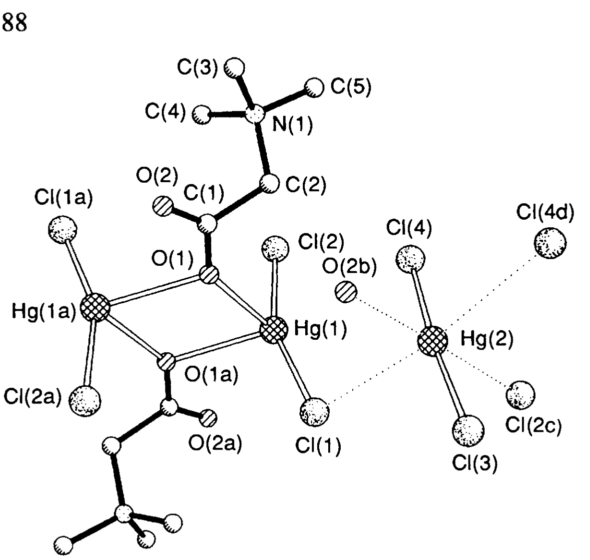

Fig. 1 Perspective view showing the co-ordination environment of the mercury(II) atoms in $[\{Hg_2L^1{}_2Cl_4\cdot 2HgCl_2\}_n]$ **1** and the atom numbering scheme. The secondary bonds are represented by dotted lines. Symmetry codes are as given in Table 3

link between the metal atoms in metal carboxylate structures, one example being the dimeric $[Hg_2(MeCO_2)_4\{P(C_6H_{11})_3\}_2]$,[25] in which one acetate group acts in the O-bridging mode and the other in the unidentate mode. Frequently the other carboxy oxygen atom O′ is also bound to another metal atom, resulting in a μ-O,O′ mode,[23b] which commonly occurs in silver(I) complexes of carboxylates and betaines.[17] Thus the O-bridging mode found in complex **1** is uncommon.

In the $HgCl_2$ unit, considering the strong covalent Hg–Cl bonds [2.276(5), 2.312(4) Å] as axial, the metal atom forms four secondary bonds in the equatorial plane with three chlorine atoms [Hg···Cl 3.083(5)–3.199(6) Å] and the O(2) atom [Hg···O 2.78(2) Å] of the carboxylato group from adjacent dimers. Thus the co-ordination geometry about the Hg(2) atom may be described as a compressed octahedron in which the most distorted angles are Cl(3)–Hg(2)–Cl(4) at 174.0(2)° and Cl(3)–Hg(2)···Cl(1) at 94.9(4)°. The secondary bonding links the dimeric and $HgCl_2$ units into a two-dimensional polymeric network concentrated about the plane $z = \frac{1}{2}$, as illustrated in Fig. 2.

$[\{Hg_2L^2{}_2Cl_4\cdot HgCl_2\}_n]$ **2**.—Complex **2** is also composed primarily of centrosymmetrical $Hg_2L^2{}_2Cl_4$ dimers and linear $HgCl_2$ units (Fig. 3). In the dimeric unit a pair of metal atoms are bridged by two oxygen atoms of the carboxylato groups [Hg–O 2.59(1), 2.66(1) Å] at an intradimer non-bonded metal–metal separation of 4.106(3) Å, while the other carboxylato oxygen atom O(2) [Hg–O(2) 2.60(1) Å] also participates in co-ordination to Hg(1). The co-ordination sphere about each metal atom in the dimer is completed by two terminal chloro ligands [2.311(7), 2.318(5) Å] in a highly irregular five-co-ordinate arrangement. The most distorted angles, as in the case of complex **1**, are Cl(1)–Hg(1)–Cl(2) 156.2(2)° and O(1)–Hg(1)–O(2) 49.9(4)°, which can also be ascribed to the stronger σ-donating ability of the chlorine atom than that of the carboxylate oxygen atom.

It is noteworthy that the carboxylato group in complex **2** acts in the very uncommon chelating plus bridging mode, which is extremely rare among metal carboxylates,[23b,26] and has not yet been found among metal complexes of betaines. Hitherto the only known examples exist in a uranyl carboxylate, $[\{UO_2(NO_3)\}_2(sal)_2]\cdot 2NC_5H_4NMe_2\text{-}4$ (sal = salicylate),[27] and a cadmium(II) carboxylate, $[\{Cd(MeCO_2)_2(H_2O)_2\}_n]$.[28] Presumably this unusual ligation mode may occur when the carboxylato group co-ordinates to metal ions of large radii.

Since the Hg(2) atom is located at an inversion centre the $HgCl_2$ unit is exactly linear with Hg–Cl 2.295(5) Å. As in the case of complex **1**, the $HgCl_2$ unit in **2** forms four secondary bonds in the equatorial plane with two chlorine [Hg(2)···Cl(2c) 3.141(7) Å] and two oxygen atoms [Hg(2)–O(2) 2.74(1) Å] from adjacent dimeric units, resulting in a compressed octahedron. These secondary bonds connect the structural units into a two-dimensional network concentrated about the plane $z = \frac{1}{2}$, as shown in Fig. 4.

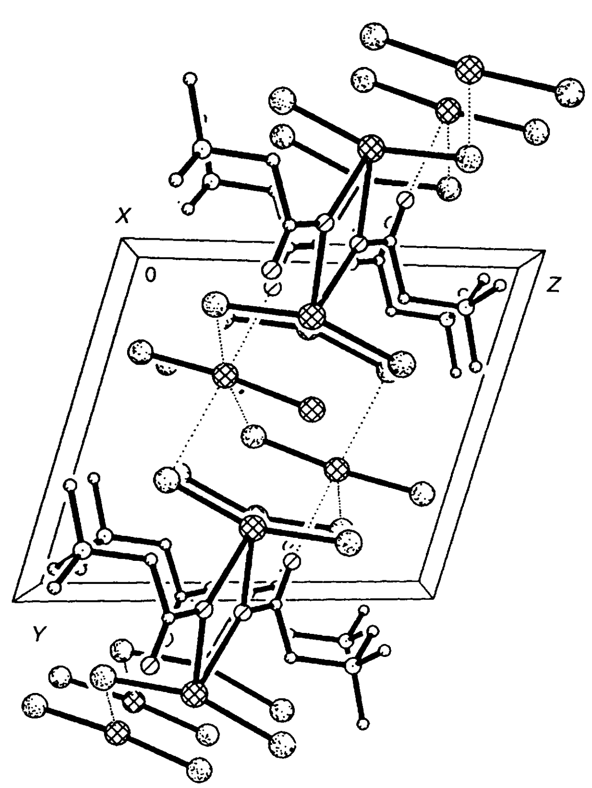

Fig. 2 Molecular packing in the crystal structure of $[\{Hg_2L^1{}_2Cl_4\cdot 2HgCl_2\}_n]$ **1**. The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downwards, and *c* from left to right. The secondary bonds are represented by dotted lines

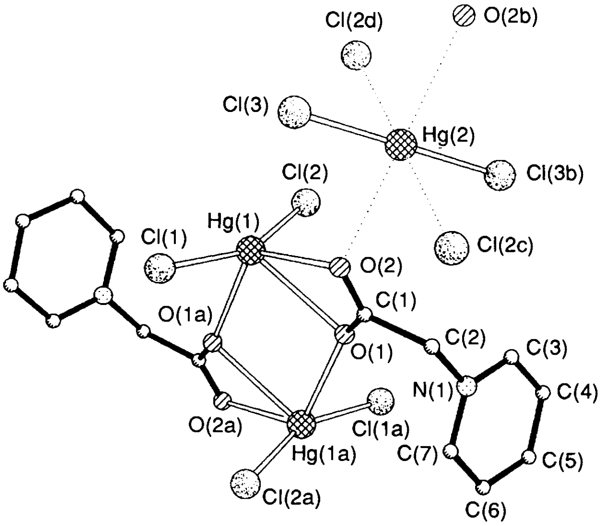

Fig. 3 Perspective view showing the co-ordination environment of the mercury(II) atoms in $[\{Hg_2L^2{}_2Cl_4\cdot HgCl_2\}_n]$ **2** and the atom numbering scheme. The secondary bonds are represented by dotted lines. Symmetry codes are as given in Table 3

$[Hg_2L^3{}_2(\mu\text{-}Cl)_2Cl_2]$ **3**.—Unlike **1** and **2**, complex **3** comprises only discrete centrosymmetrical $Hg_2L^3{}_2(\mu\text{-}Cl)_2Cl_2$ dimers (Fig. 5) in which a pair of metal atoms, separated at a non-bonded distance of 3.754(3) Å, are linked by unsymmetrical μ-chloro

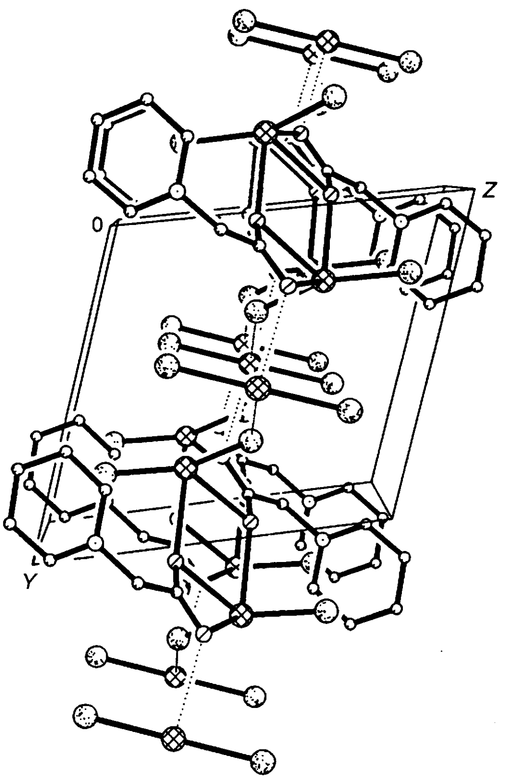

Fig. 4 Molecular packing in the crystal structure of $[\{Hg_2L^2{}_2Cl_4{\cdot}HgCl_2\}_n]$ **2**. Details as in Fig. 2

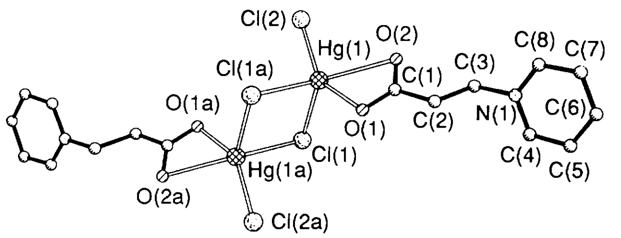

Fig. 5 Perspective view showing the molecular structure of $[Hg_2L^3{}_2(\mu\text{-}Cl)_2Cl_2]$ **3** and the atom numbering scheme. Symmetry codes are as given in Table 3

bridges [Hg–Cl 2.578(4), 2.743(3) Å]. The co-ordination sphere about each metal atom is completed by an unsymmetrical bidentate carboxylato group [Hg–O 2.191(9), 2.679(9) Å] and a terminal chloro ligand [Hg–Cl 2.358(4) Å] in a very distorted square-pyramidal geometry; regarding the Cl(1)–Hg(1) bond as axial, the most distorted angles are Cl(1a)–Hg(1)–O(2) 131.6(3)° and O(1)–Hg(1)–O(2) 51.6(5)°. The terminal Hg–Cl bond length is significantly shorter than those of the bridging Hg–Cl bonds. The Hg(1)–O(1) bond [2.191(9) Å] is significantly shorter by more than 0.35 Å than all the other Hg–O bonds in complexes **1**–**3**, although it is still longer than the longest one [2.08(1) Å] found in $[C\{Hg(MeCO_2)\}_4]{\cdot}2H_2O$,[7] where the acetato group acts in a unidentate fashion. The geometry of the chloro bridge in complex **3** is comparable to those found in a number of mercury(II) chloride adducts with phosphines.[14,15]

Complex **3** is distinct from both **1** and **2** in regard to the different co-ordination mode of the carboxylato group and the absence of $HgCl_2$ species in the crystal. This may be due to the fact that, with one more methylene group as a spacer between the pyridine ring and the carboxy group as compared to pyridinioacetate (L^2), the pyridine ring in L^3 may be further stretched, thus facilitating an optimum arrangement of ligands about each metal centre that effectively precludes association to any $HgCl_2$ species by secondary bonding.

Conclusion

The present study has shown that betaine ligands can exhibit different co-ordination modes in their mercury(II) complexes, which are uncommon in the metal carboxylates and betaine complexes of other metals. That the same product can be obtained by using different molar ratios of starting materials implies that the stoichiometry of a particular mercury(II) chloride–betaine adduct depends mainly on the ligand characteristics. The dominant factor affecting the stoichiometry might be the size of the betaine ligand, which may dictate the extent of secondary bonding between the ligands of the dimeric unit and the metal atom of the co-existing $HgCl_2$ species.

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