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Solid-state aggregation of mercury bis-acetylides, $Hg(C{\equiv}CR)_2$, R = Ph, $SiMe_3$

Suzanne J. Faville, William Henderson, Trevor J. Mathieson, Brian K. Nicholson *

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

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Abstract

The structures of $Hg(C{\equiv}CR)_2$ (R = Ph, $SiMe_3$) show unusual aggregation in the solid state. When R = Ph there are eight independent molecules in the asymmetric unit, while for R = $SiMe_3$ there are pentameric aggregates. The Hg…Hg distances are 3.7–4.0 Å, possibly indicating weak mercuriophilic interactions, but the main driving force for clustering appears to be interactions between Hg atoms and the C≡C bonds of adjacent molecules. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Mercury; Acetylides; Mercuriophilic interactions; Aggregation

1. Introduction

It is now widely recognised that Au(I) complexes often form solid-state structures which involve attractive secondary interactions, the auriophilic effect. [1–6]. The Au…Au distances are typically 3.0–3.6 Å, longer than the Au–Au distance in gold metal but shorter than the sum of the van der Waals radii. Theoretical analysis has attributed this to electron correlation enhanced by relativistic effects [5,6].

For other d^{10} ions there are fewer examples of similar interactions, as reviewed by Pyykkö [5]. For Hg^{2+} in particular, evidence for intermetallic bonding interactions is not strong. An early example comes from the structure determination of $Hg(CH_2Ph)_2$ in which the molecules are stacked in a linear chain with Hg…Hg distances of 3.54 Å [7]. Although it wasn't commented on at the time, this represents reasonable evidence for mercuriophilicity. Similarly the packing in MeHgCN is of the zig-zag chain type with Hg…Hg 3.77 Å [8], very similar to packing in gold(I) complexes such as (Bu^tNC)AuX, (X = Cl, NO_3) for example [9,10]. The *ortho*-phenylene-mercury trimer has intramolecular Hg…Hg distances of 3.44 Å [11]. A more recent example involving a uracil-Hg(II) complex has been described, with Hg…Hg distances in the range 3.47–3.67 Å [12].

In an effort to find other examples of this type we have determined the structures of two mercury(II) acetylides, $Hg(C{\equiv}CR)_2$. These were chosen because they have sterically unhindered Hg centres, are non-polar, and contain no obvious Lewis base sites for intermolecular bonding in the solid state. Surprisingly, no structures of simple two-coordinate mercury bis-acetylides have been described before [13], despite their ease of preparation [14] and widespread application in synthesis [15].

2. Experimental

2.1. Preparations

$Hg(C{\equiv}CPh)_2$ was prepared from $[HgI_4]^{2-}$ and PhCCH using the well-established route [14], while $Hg(C{\equiv}CSiMe_3)_2$ was prepared from the reaction of $Li[C{\equiv}CSiMe_3]$ (from Me_3SiCCH and BuLi in Et_2O)

* Corresponding author. Fax: +64-7-8384219.
E-mail address: b.nicholson@waikato.ac.nz (B.K. Nicholson)

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Table 1
Atomic coordinates and equivalent isotropic displacement parameters for $Hg(CCPh)_2$

	x	y	z	U_{eq}
Hg(1)	0.3482(1)	0.5440(1)	0.0284(1)	0.030(1)
Hg(2)	0.1524(1)	0.5413(1)	−0.0427(1)	0.031(1)
Hg(3)	0.0363(1)	0.9609(1)	−0.0525(1)	0.036(1)
Hg(4)	0.4449(1)	0.9498(1)	0.0683(1)	0.037(1)
Hg(5)	0.2149(1)	0.6939(1)	0.0474(1)	0.033(1)
Hg(6)	0.4084(1)	0.7432(1)	0.0590(1)	0.030(1)
Hg(7)	0.2479(1)	0.8984(1)	0.0028(1)	0.036(1)
Hg(8)	0.0814(1)	0.7480(1)	−0.0619(1)	0.032(1)
C(11)	0.2710(10)	0.5112(12)	0.0554(6)	0.033(5)
C(12)	0.2323(9)	0.4879(11)	0.0767(6)	0.028(4)
C(111)	0.1930(9)	0.4557(11)	0.1051(6)	0.026(4)
C(112)	0.2289(11)	0.4260(12)	0.1473(6)	0.035(5)
C(113)	0.1899(10)	0.3934(12)	0.1735(6)	0.034(5)
C(114)	0.1167(11)	0.3843(12)	0.1582(7)	0.036(5)
C(115)	0.0825(11)	0.4159(13)	0.1170(8)	0.046(6)
C(116)	0.1187(10)	0.4485(11)	0.0908(6)	0.027(4)
C(13)	0.4308(10)	0.5783(11)	0.0057(6)	0.029(4)
C(14)	0.4789(9)	0.5996(11)	−0.0075(6)	0.027(4)
C(121)	0.5381(9)	0.6229(11)	−0.0242(6)	0.029(5)
C(122)	0.5918(10)	0.6682(13)	0.0025(8)	0.045(6)
C(123)	0.6503(12)	0.6916(16)	−0.0125(9)	0.062(7)
C(124)	0.6511(14)	0.6754(18)	−0.0554(10)	0.070(8)
C(125)	0.5960(15)	0.6292(14)	−0.0825(8)	0.055(7)
C(126)	0.5390(10)	0.6075(12)	−0.0664(7)	0.034(5)
C(21)	0.0822(10)	0.5820(12)	−0.0114(6)	0.030(5)
C(22)	0.0397(11)	0.6001(12)	0.0072(6)	0.033(5)
C(211)	−0.0113(10)	0.6208(11)	0.0321(7)	0.034(5)
C(212)	−0.0794(11)	0.6464(13)	0.0119(8)	0.043(6)
C(213)	−0.1267(12)	0.6603(16)	0.0359(11)	0.062(8)
C(214)	−0.1087(13)	0.6509(15)	0.0796(12)	0.064(8)
C(215)	−0.0406(13)	0.6261(14)	0.1025(8)	0.053(6)
C(216)	0.0071(12)	0.6101(12)	0.0777(7)	0.041(5)
C(23)	0.2240(10)	0.5015(14)	−0.0720(7)	0.042(6)
C(24)	0.2651(9)	0.4780(11)	−0.0914(6)	0.030(5)
C(221)	0.3154(9)	0.4478(11)	−0.1150(6)	0.028(4)
C(222)	0.2898(10)	0.4212(13)	−0.1577(7)	0.041(5)
C(223)	0.3363(13)	0.3953(18)	−0.1797(9)	0.072(9)
C(224)	0.4077(12)	0.3952(16)	−0.1605(9)	0.061(8)
C(225)	0.4343(10)	0.4220(13)	−0.1179(7)	0.042(6)
C(226)	0.3881(10)	0.4473(12)	−0.0954(6)	0.034(5)
C(31)	0.0895(12)	1.0279(12)	−0.0022(7)	0.041(5)
C(32)	0.1274(11)	1.0691(12)	0.0256(6)	0.034(5)
C(311)	0.1698(10)	1.1154(11)	0.0580(7)	0.031(5)
C(312)	0.1458(10)	1.1930(10)	0.0636(7)	0.031(5)
C(313)	0.1874(12)	1.2381(12)	0.0949(8)	0.041(5)
C(314)	0.2524(13)	1.2168(13)	0.1200(8)	0.050(6)
C(315)	0.2756(15)	1.1441(16)	0.1165(10)	0.083(10)
C(316)	0.2350(13)	1.0962(14)	0.0839(9)	0.060(7)
C(33)	−0.0118(13)	0.8977(14)	−0.1052(7)	0.047(6)
C(34)	−0.0382(10)	0.8632(13)	−0.1387(7)	0.037(5)
C(321)	−0.0713(13)	0.8276(15)	−0.1807(8)	0.054(7)
C(322)	−0.1461(14)	0.8261(16)	−0.1989(10)	0.078(10)
C(323)	−0.1746(18)	0.795(2)	−0.2441(16)	0.12(2)
C(324)	−0.127(3)	0.772(2)	−0.2629(18)	0.16(3)
C(325)	−0.057(2)	0.7674(17)	−0.2476(9)	0.088(11)
C(326)	−0.0298(17)	0.7954(15)	−0.2057(9)	0.066(8)
C(41)	0.3933(11)	1.0201(12)	0.0206(7)	0.036(5)
C(42)	0.3608(10)	1.0625(12)	−0.0070(7)	0.035(5)
C(411)	0.3243(10)	1.1181(12)	−0.0409(7)	0.035(5)
C(412)	0.3632(10)	1.1572(12)	−0.0658(7)	0.036(5)
C(413)	0.3294(11)	1.2074(13)	−0.0978(7)	0.042(6)
C(414)	0.2571(16)	1.2204(14)	−0.1052(8)	0.061(8)
C(415)	0.2175(12)	1.1826(13)	−0.0806(7)	0.044(6)
C(416)	0.2525(10)	1.1312(12)	−0.0483(7)	0.040(5)
C(43)	0.4926(11)	0.8825(13)	0.1197(7)	0.040(5)
C(44)	0.5135(10)	0.8478(12)	0.1533(7)	0.033(5)
C(421)	0.5369(10)	0.8044(13)	0.1943(7)	0.037(5)
C(422)	0.6101(11)	0.7992(15)	0.2156(8)	0.051(6)
C(423)	0.6299(12)	0.7610(16)	0.2550(8)	0.057(7)
C(424)	0.5805(13)	0.7275(16)	0.2740(8)	0.064(8)
C(425)	0.5092(14)	0.7327(17)	0.2529(8)	0.066(8)
C(426)	0.4879(11)	0.7716(13)	0.2130(7)	0.046(6)
C(51)	0.1870(11)	0.6882(13)	0.1036(8)	0.043(6)
C(52)	0.1704(10)	0.6839(12)	0.1389(7)	0.033(5)
C(511)	0.1527(9)	0.6726(11)	0.1794(6)	0.027(4)
C(512)	0.1473(15)	0.6013(18)	0.1931(11)	0.079(10)
C(513)	0.1303(17)	0.589(3)	0.2321(13)	0.114(17)
C(514)	0.130(2)	0.646(3)	0.2607(9)	0.125(19)
C(515)	0.1304(19)	0.721(2)	0.2463(13)	0.095(12)
C(516)	0.1451(17)	0.7324(17)	0.2055(10)	0.079(9)
C(53)	0.2454(10)	0.7008(13)	−0.0086(7)	0.036(5)
C(54)	0.2628(10)	0.7097(12)	−0.0427(8)	0.039(6)
C(521)	0.2859(10)	0.7153(12)	−0.0832(6)	0.031(5)
C(522)	0.3317(11)	0.6597(16)	−0.0937(7)	0.052(7)
C(523)	0.3558(12)	0.6705(18)	−0.1304(8)	0.062(8)
C(524)	0.3312(12)	0.7352(18)	−0.1585(7)	0.059(8)
C(525)	0.2851(17)	0.7829(14)	−0.1482(8)	0.063(8)
C(526)	0.2603(14)	0.7755(13)	−0.1113(8)	0.052(6)
C(61)	0.3934(10)	0.6757(14)	0.1070(6)	0.037(5)
C(62)	0.3878(10)	0.6346(13)	0.1366(6)	0.034(5)
C(611)	0.3852(10)	0.5869(12)	0.1737(6)	0.032(5)
C(612)	0.4253(11)	0.5230(12)	0.1833(7)	0.040(5)
C(613)	0.4232(11)	0.4773(13)	0.2189(8)	0.047(6)
C(614)	0.3823(13)	0.4989(13)	0.2459(8)	0.048(6)
C(615)	0.3405(13)	0.5635(14)	0.2376(8)	0.050(6)
C(616)	0.3432(11)	0.6072(15)	0.2016(7)	0.048(6)
C(63)	0.4257(11)	0.8053(13)	0.0096(7)	0.035(5)
C(64)	0.4352(9)	0.8295(10)	−0.0238(7)	0.028(5)
C(621)	0.4493(10)	0.8580(12)	−0.0647(6)	0.031(5)
C(622)	0.4994(12)	0.8198(13)	−0.0809(7)	0.041(5)
C(623)	0.5118(13)	0.8421(14)	−0.1204(8)	0.054(7)
C(624)	0.4738(13)	0.9049(16)	−0.1436(8)	0.060(7)
C(625)	0.4244(12)	0.9417(14)	−0.1271(7)	0.047(6)
C(626)	0.4113(10)	0.9177(11)	−0.0874(7)	0.033(5)
C(71)	0.2887(9)	0.8799(12)	0.0692(7)	0.032(5)
C(72)	0.3043(9)	0.8844(10)	0.1084(6)	0.026(4)
C(711)	0.3235(10)	0.8919(11)	0.1547(6)	0.028(4)
C(712)	0.3651(11)	0.9520(13)	0.1760(7)	0.044(6)
C(713)	0.3803(15)	0.9620(19)	0.2206(8)	0.072(9)
C(714)	0.3520(15)	0.913(2)	0.2457(9)	0.075(9)
C(715)	0.3089(14)	0.8532(17)	0.2258(8)	0.062(7)
C(716)	0.2960(11)	0.8440(16)	0.1807(7)	0.049(6)
C(73)	0.2088(10)	0.9277(12)	−0.0614(6)	0.034(5)
C(74)	0.1917(10)	0.9593(11)	−0.0963(6)	0.029(4)
C(721)	0.1773(9)	0.9985(10)	−0.1368(6)	0.026(4)
C(722)	0.2335(12)	1.0287(16)	−0.1522(8)	0.059(7)
C(723)	0.2204(18)	1.0679(18)	−0.1906(9)	0.075(9)
C(724)	0.1529(15)	1.0869(13)	−0.2137(8)	0.054(7)
C(725)	0.0979(14)	1.0625(17)	−0.1990(8)	0.066(8)
C(726)	0.1095(11)	1.0157(17)	−0.1611(7)	0.060(8)
C(81)	0.0792(9)	0.8042(11)	−0.0064(6)	0.025(4)
C(82)	0.0748(9)	0.8283(12)	0.0281(7)	0.030(5)
C(811)	0.0669(10)	0.8545(10)	0.0715(6)	0.025(4)
C(812)	0.1153(11)	0.9073(12)	0.0961(7)	0.037(5)
C(813)	0.1094(10)	0.9296(13)	0.1369(7)	0.041(6)
C(814)	0.0543(11)	0.9049(15)	0.1520(7)	0.049(6)
C(815)	0.0059(13)	0.8513(17)	0.1269(8)	0.061(8)
C(816)	0.0128(12)	0.8261(17)	0.0872(8)	0.060(7)
C(83)	0.0860(9)	0.6843(9)	−0.1145(5)	0.022(4)
C(84)	0.0943(9)	0.6444(12)	−0.1420(7)	0.032(5)
C(821)	0.1029(10)	0.5903(12)	−0.1750(6)	0.031(5)
C(822)	0.1603(12)	0.5968(13)	−0.1938(8)	0.046(6)
C(823)	0.1667(14)	0.5509(18)	−0.2257(8)	0.066(8)
C(824)	0.1184(14)	0.4919(15)	−0.2414(9)	0.059(7)
C(825)	0.0632(14)	0.4837(16)	−0.2221(9)	0.072(9)
C(826)	0.0527(12)	0.5314(16)	−0.1909(8)	0.059(7)

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Hg(CCSiMe_3)_2$

	x	y	z	U_{eq}
Hg(1)	0.1979(1)	0.2314(1)	0.0930(1)	0.042(1)
Si(12)	0.4689(3)	0.2248(2)	0.2876(2)	0.045(1)
Si(11)	−0.0880(3)	0.2248(2)	−0.0956(2)	0.055(1)
C(10)	0.0840(12)	0.2302(6)	0.0149(7)	0.042(4)
C(11)	0.0200(12)	0.2301(7)	−0.0298(6)	0.054(5)
C(12)	−0.2106(13)	0.2289(10)	−0.0731(8)	0.115(9)
C(13)	−0.0773(14)	0.1591(7)	−0.1289(8)	0.086(6)
C(14)	−0.0802(14)	0.2792(7)	−0.1476(6)	0.073(6)
C(15)	0.3071(12)	0.2345(6)	0.1707(6)	0.047(4)
C(16)	0.3690(12)	0.2343(7)	0.2169(6)	0.054(5)
C(17)	0.5941(11)	0.2299(7)	0.2710(6)	0.066(5)
C(18)	0.4612(13)	0.2763(7)	0.3414(7)	0.070(5)
C(19)	0.4458(14)	0.1581(8)	0.3145(8)	0.088(7)
Hg(2)	0.2616(1)	0.3563(1)	0.1845(1)	0.044(1)
Si(21)	0.6068(3)	0.4360(2)	0.2789(2)	0.051(1)
Si(22)	−0.1098(3)	0.3060(2)	0.1308(2)	0.057(1)
C(20)	0.4000(12)	0.3856(6)	0.2196(6)	0.046(4)
C(21)	0.4834(13)	0.4045(6)	0.2431(6)	0.047(4)
C(22)	0.5875(14)	0.5087(7)	0.2733(9)	0.082(6)
C(23)	0.6451(14)	0.4169(8)	0.3569(7)	0.083(6)
C(24)	0.7012(12)	0.4109(7)	0.2421(7)	0.067(5)
C(25)	0.1171(11)	0.3345(6)	0.1547(6)	0.044(4)
C(26)	0.0263(12)	0.3207(6)	0.1392(6)	0.048(4)
C(27)	−0.1278(14)	0.2944(9)	0.2041(7)	0.096(7)
C(28)	−0.1819(14)	0.3643(10)	0.0976(10)	0.137(12)
C(29)	−0.1401(18)	0.2443(12)	0.0860(12)	0.175(15)
Hg(3)	0.0923(1)	0.3599(1)	0.0080(1)	0.046(1)
Si(31)	−0.2405(3)	0.4449(2)	−0.0958(2)	0.056(1)
Si(32)	0.4736(3)	0.3440(2)	0.0639(2)	0.049(1)
C(30)	−0.0501(12)	0.3863(6)	−0.0299(7)	0.050(4)
C(31)	−0.1266(13)	0.4080(6)	−0.0558(7)	0.058(5)
C(32)	−0.2885(13)	0.4174(8)	−0.1716(7)	0.082(6)
C(33)	−0.3404(14)	0.4409(9)	−0.0558(8)	0.097(7)
C(34)	−0.2035(16)	0.5134(6)	−0.0987(8)	0.087(7)
C(35)	0.2407(12)	0.3446(6)	0.0410(6)	0.045(4)
C(36)	0.3355(13)	0.3414(6)	0.0536(6)	0.046(4)
C(37)	0.4985(13)	0.3197(7)	−0.0063(7)	0.068(5)
C(38)	0.5375(11)	0.3004(7)	0.1263(7)	0.062(5)
C(39)	0.5102(13)	0.4148(7)	0.0770(7)	0.066(5)
Hg(4)	0.2541(1)	0.2519(1)	−0.0600(1)	0.047(1)
Si(41)	0.1280(5)	0.4277(2)	−0.1524(2)	0.072(2)
Si(42)	0.4826(5)	0.1135(2)	0.0620(2)	0.080(2)
C(40)	0.1930(11)	0.3166(6)	−0.1058(7)	0.041(4)
C(41)	0.1626(12)	0.3594(7)	−0.1249(6)	0.048(4)
C(42)	−0.0049(16)	0.4248(9)	−0.1985(10)	0.113(9)
C(43)	0.150(2)	0.4716(8)	−0.0830(9)	0.139(11)
C(44)	0.2182(17)	0.4496(8)	−0.1952(9)	0.099(7)
C(45)	0.3333(12)	0.1949(6)	−0.0100(7)	0.044(4)
C(46)	0.3909(13)	0.1619(6)	0.0209(7)	0.053(4)
C(47)	0.5993(19)	0.1179(13)	0.0345(13)	0.181(14)
C(48)	0.431(2)	0.0487(9)	0.0509(10)	0.130(10)
C(49)	0.513(2)	0.1304(8)	0.1405(8)	0.133(11)
Hg(5)	0.1404(1)	0.2678(1)	−0.2479(1)	0.050(1)
Si(51)	0.2278(4)	0.0898(2)	−0.1476(2)	0.062(1)
Si(52)	0.0455(6)	0.4215(2)	−0.3905(2)	0.093(2)
C(50)	0.1794(11)	0.2022(7)	−0.1987(7)	0.051(4)
C(51)	0.1975(12)	0.1570(7)	−0.1740(7)	0.055(5)
C(52)	0.1670(19)	0.0448(8)	−0.2107(8)	0.112(9)
C(53)	0.3655(15)	0.0809(9)	−0.1257(9)	0.094(7)
C(54)	0.1712(14)	0.0772(8)	−0.0849(7)	0.081(6)
C(55)	0.0997(12)	0.3304(7)	−0.3022(6)	0.049(4)
C(56)	0.0739(15)	0.3681(7)	−0.3374(8)	0.070(6)
C(57)	0.0630(16)	0.4858(7)	−0.3523(8)	0.094(7)
C(58)	0.144(4)	0.4195(11)	−0.4327(14)	0.31(3)
C(59)	−0.078(3)	0.4111(13)	−0.4393(19)	0.37(4)

with $HgCl_2$. Physical and spectroscopic properties were in full accord with those in the literature [16].

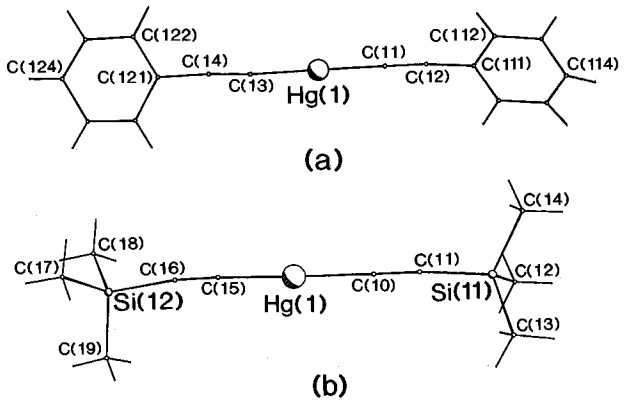

Fig. 1. Views of individual molecules of (a) $Hg(C{\equiv}CPh)_2$ and (b) $Hg(C{\equiv}CSiMe_3)_2$, showing numbering system. Other independent molecules are numbered accordingly. For $Hg(CCPh)_2$ average bond lengths are Hg–C 2.00(2) Å, C≡C 1.19(3) Å, and the C–Hg–C angles are 174.3–178.6°. For $Hg(CCSiMe_3)_2$ average bond lengths are 2.00(2), C≡C 1.22(2) Å, with C–Hg–C 170.8–178.1°.

2.2. X-ray crystallography

Unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo–K_α X-rays (0.71073 Å). Corrections for absorption and other effects was carried out with SADABS [17] and all other calculations used the SHELX97 programs [18]. The positions of the Hg atoms were located by direct methods, and the full structures were developed in the usual manner. Final refinement was based on F^2. All non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions. Refined coordinates are given in Tables 1 and 2, while selected bond parameters are summarised in the caption to Fig. 1. Hg…Hg distances are included in the caption to Fig. 3.

2.2.1. Data for $Hg(C{\equiv}CPh)_2$

Crystals were obtained from slow diffusion of hexane into a solution of $Hg(C{\equiv}CPh)_2$ in benzene. $C_{16}H_{10}Hg$, M_r 402.83, monoclinic, $P2_1/c$, $a = 19.442(3)$, $b = 17.677(2)$, $c = 31.346(4)$ Å, $\beta = 105.68(1)$, $V = 10372(2)$ Å^3, $D_{calc} = 2.064$ g cm^{-3}, $Z = 32$, $F(000) = 5952$, μ(Mo–K_α) 11.8 mm^{-1}, T_{max} 0.1557, T_{min} 0.0521, crystal size $0.61 \times 0.33 \times 0.25$ mm^3, $T = 158$ K. A total of 37628 reflections, 15791 unique (R_{int} 0.0385) in the range $2° < \theta < 24°$ was used for all calculations. Final R_1 0.0883 (14724 data with $I > 2\sigma(I)$), 0.0969 (all data), wR_2 0.1482, GoF 1.537, final Δe +1.96/−1.86 e Å^{-3}.

2.2.2. Data for $Hg(C{\equiv}CSiMe_3)_2$

Crystals were obtained by cooling a saturated hexane solution of $Hg(C{\equiv}CSiMe_3)_2$ to −20°C. $C_{10}H_{18}HgSi_2$, M_r 395.01, monoclinic, $P2_1/c$, $a =$

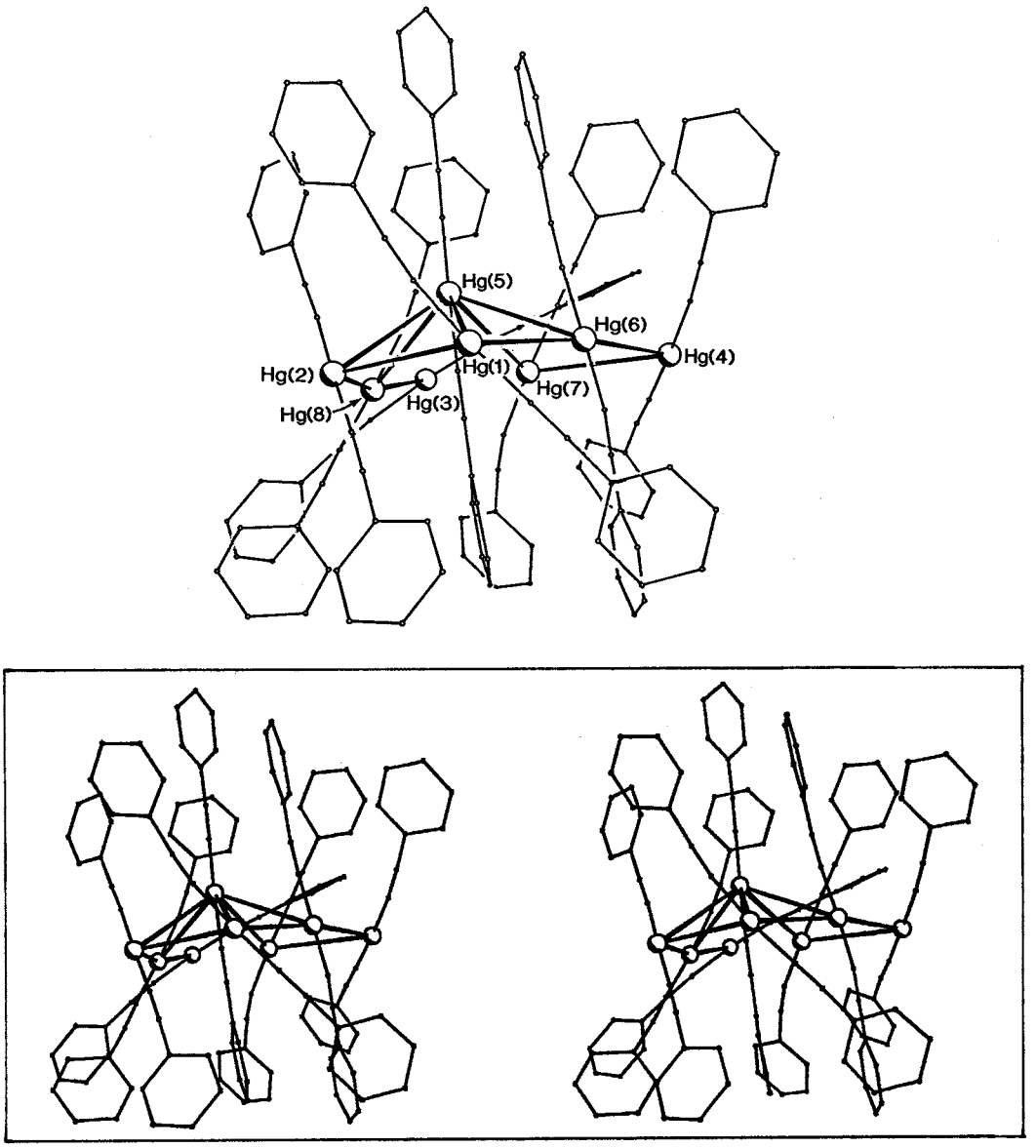

Fig. 2. A general and a stereo view of $Hg(C{\equiv}CPh)_2$ showing the arrangement of the molecules in the octameric aggregate.

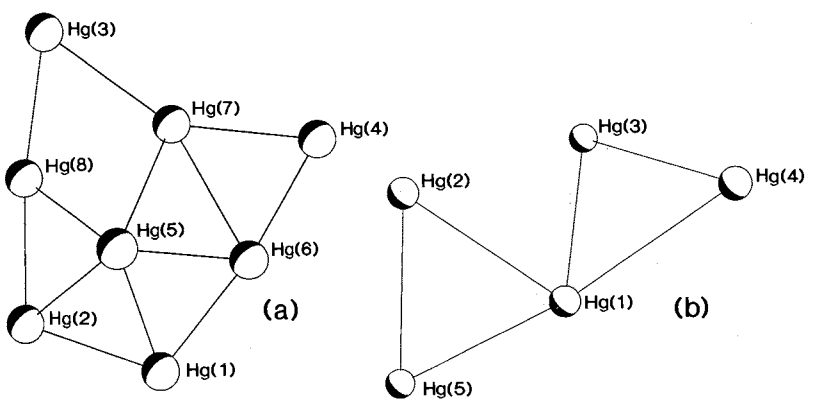

Fig. 3. Representations of the relative positions of the Hg atoms in the aggregates for (a) $Hg(C{\equiv}CPh)_2$ and (b) $Hg(C{\equiv}CSiMe_3)_2$. Hg…Hg distances (Å) are: for $Hg(C{\equiv}CPh)_2$; Hg(1)…Hg(2) 3.85, Hg(1)…Hg(5) 3.86, Hg(1)…Hg(6) 3.75, Hg(2)…Hg(5) 3.86, Hg(2)…Hg(8) 3.89, Hg(5)…Hg(6) 3.78, Hg(5)…Hg(7) 3.99, Hg(5)…Hg(8) 3.81, Hg(6)…Hg(7) 4.17, Hg(4)…Hg(6) 3.71, Hg(4)…Hg(7) 3.93, Hg(3)…Hg(7) 4.16, Hg(7)…Hg(8) 4.25, Hg(3)…Hg(7) 4.16, Hg(3)…Hg(8) 3.89, Hg(3)…Hg(3)′ 4.15; and for $Hg(C{\equiv}CSiMe_3)_2$: Hg(1)…Hg(2) 3.76, Hg(1)…Hg(3) 3.85, Hg(1)…Hg(4) 3.90, Hg(1)…Hg(5) 4.01, Hg(2)…Hg(5) 4.03, Hg(3)…Hg(4) 4.07.

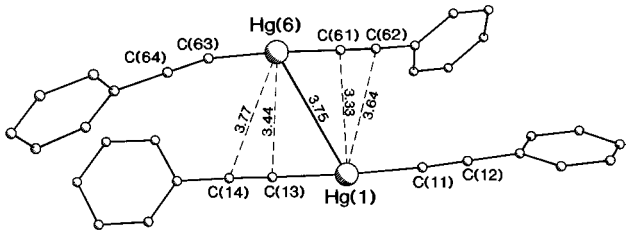

Fig. 4. A diagram showing the typical relationship between adjacent molecules, indicating attractions of both Hg...Hg and Hg-η^2-C≡C types. Distances are in Å.

13.5811(4), $b = 25.0300(8)$, $c = 23.5038(7)$ Å, $\beta = 105.35(1)$, $V = 7704.8(4)$ Å^3, $D_{calc} = 1.703$ g cm^{-3}, $Z = 20$, $F(000) = 3720$, μ(Mo–K_α) 10.1 mm^{-1}, T_{max} 0.2903, T_{min} 0.1411, crystal size $0.65 \times 0.25 \times 0.15$ mm^3, $T = 203$ K. A total of 67399 reflections, 15800 unique (R_{int} 0.0851) in the range $2° < \theta < 28°$ was collected. Higher angle data were weak so the 12106 independent reflections with $2\theta < 48°$ were used for all calculations. Final R_1 0.0625 (7339 data with $I = 2\sigma(I)$), 0.1186 (all data), wR_2 0.1471, GoF 1.018, final Δe $+2.92/-3.11$ e Å^{-3}.

3. Results and discussion

The crystal structure of $Hg(C{\equiv}CPh)_2$ showed that there were *eight* independent molecules in the asymmetric unit, quite remarkable in view of the intrinsic high symmetry of an isolated molecule. Individual molecules consisted of the expected linearly-coordinated mercury (Fig. 1(a)), and the eight examples differed only in relative orientations of the C_6H_5 rings, and in small variations in bond angles. The complicated interactions between the molecules are shown in Fig. 2. The arrangement is such that the mercury atoms Hg(1), Hg(2), Hg(6), Hg(7) and Hg(8) form an irregular pentagon, with Hg(5) in the centre (though displaced above the Hg_5 ring), while Hg(3) and Hg(4) bridge two of the

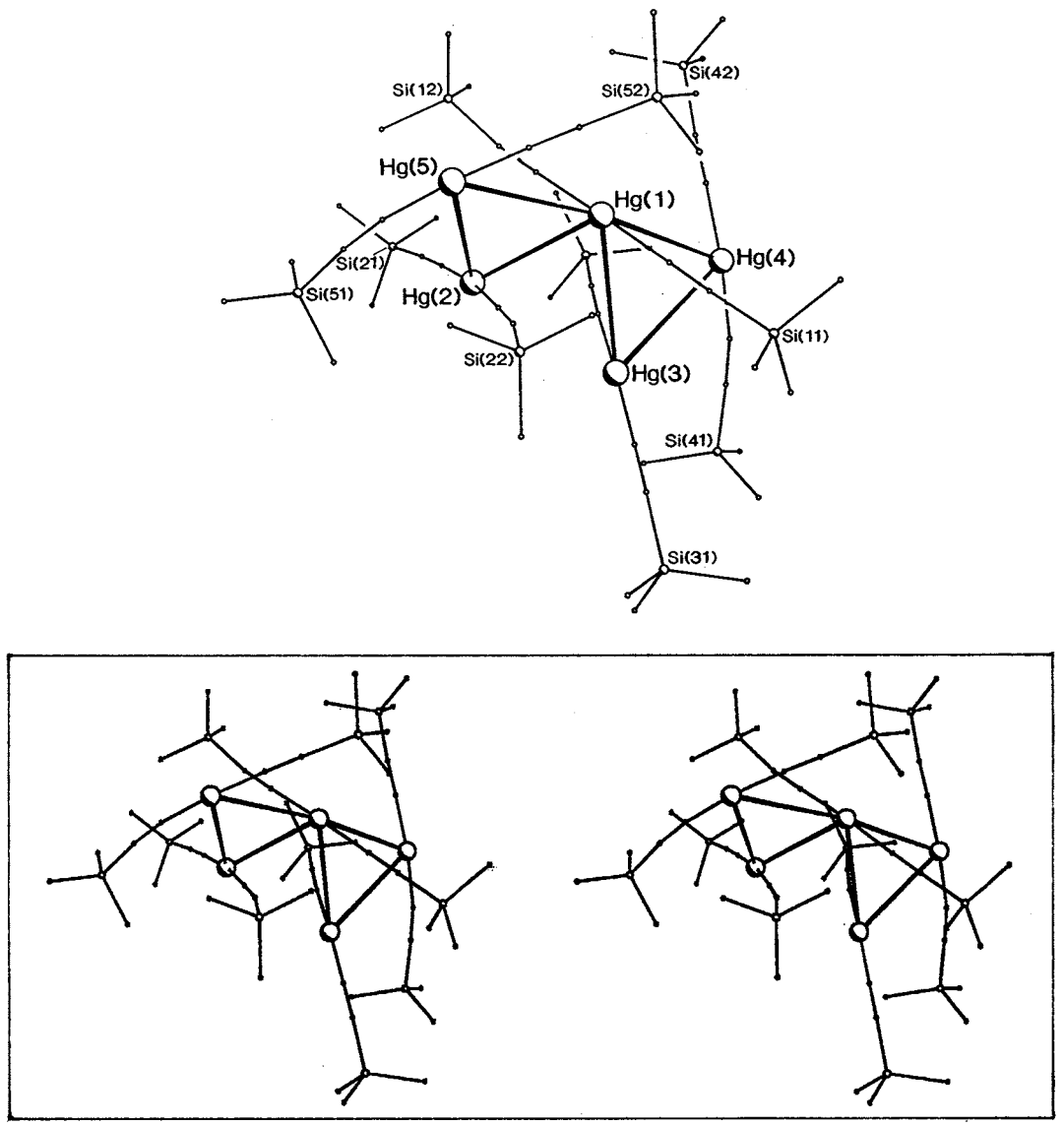

Fig. 5. A perspective and a stereo view of the pentameric unit of $Hg(C{\equiv}CSiMe_3)_2$.

edges (Fig. 3(a)). These units are linked to symmetry related ones through Hg(3)…Hg(3)′ vectors.

This description does not imply strong Hg…Hg mercuriophilic bonds, since the distances range from 3.7 to over 4.0 Å. These are towards the upper limit of distances accepted as representing metallophilic interactions, although a recent estimate of the Van der Waals radius of mercury gives a value as high as 2.0 Å [5,19]. A more detailed examination of the clusters reveals an additional explanation for the aggregation. Each Hg is adjacent to the C≡C bond of neighbouring molecules, which are orientated to maximise the interaction of the triple bond with the metal. The detailed arrangements are complicated—for example Hg(5) is surrounded by the C≡C bonds of five separate monomers. Fig. 4 shows a typical arrangement of adjacent molecules, and suggests that the packing is also influenced by the tendency that d^{10} ions have for forming η^2 bonds to triple bonds. However this does not preclude Hg…Hg bonding. The intermolecular distances from the Hg atoms to C_α are around 3.3–3.4 Å, and to C_β about 3.6–3.7 Å. The sum of the Van der Waals radii for Hg and C is approximately 3.7 Å, so distances in this range do indicate a definite interaction. The closest precedents for η^2-C≡C interactions to Hg(II) in the literature are the HgX_2 (X = Cl, Br) adducts of anionic platinum complexes $[L_2Pt(C{\equiv}CSiMe_3)_2]^{2-}$; however, in contrast the Hg for these examples is closest to the C_β atom (Hg…C_α 2.60–2.73 Å, Hg…C_β 2.43–2.53 Å [20]). Also related are Au…C distances of 2.123–2.259 Å in η^2-C≡C linkages in the aggregate $[\{Au(C{\equiv}CBu^t)\}_6]_2$ [21], and 2.21–2.27 Å in the [AuR] adducts of the tweezer molecules $Cp_2Ti(C{\equiv}CSiMe_3)_2$ [22]. In a comparable $[Au(C{\equiv}CR)_2]^-$ (R = CH_2OH) structure there is no significant interaction between the anions, presumably because of the net charge and the presence of the PPN^+ counterion in the lattice [23].

For $Hg(C{\equiv}CPh)_2$ the Hg atoms in each case project onto the midpoint of the neighbouring Hg–C≡C unit, closest to C_α, which would argue against the intermolecular η^2 interaction dominating the packing since small shifts would allow more equal Hg…C_α and Hg…C_β distances. Rather there seems to be a combination of Hg…Hg and Hg…C_2 attractions.

The structure of $Hg(C{\equiv}CSiMe_3)_2$ was also determined to see if similar interactions occurred. Individual molecules are again essentially linear (Fig. 1(b)). However, in this case there are five molecules aggregated together such that the five mercury atoms form two triangles with a common vertex, twisted so that the dihedral angle between the planes is 45° (Fig. 3(b)). As for the previous example, the Hg…Hg distances are in the range 3.76–4.0 Å and the orientation of the acetylide ligands (Fig. 5) is once more such that the C≡C bonds are inclined towards the mercury atoms of adjacent molecules. Each Hg interacts with 2–3 adjacent Hg–C≡C units, if it is taken that a Hg–C_α distance of less than 3.5 Å is significant. The range of values is 3.14–3.48 (average 3.34 Å) for C_α and 3.38–3.63 (average 3.51 Å) for Hg–C_β. Once again it suggests that the interaction is over the whole Hg–C≡C unit, centered on C_α rather than being a purely η^2-C≡C type. The compound $[Au(C{\equiv}CSiMe_3)(CNBu^t)]$ forms a related trameric aggregate with a central Au surrounded by three others, aggregated by Au…Au interactions alone [23].

4. Conclusion

Whatever the origin of the attractive forces, there is clearly a strong tendency for $Hg(C{\equiv}CR)_2$ molecules to aggregate together, since both examples considered here of simple symmetric molecules have adopted a complicated structure. The interactions between molecules are apparently sufficient to preclude perhaps more expected packing, such as π–π stacking of the arene rings of $Hg(C{\equiv}CPh)_2$ for example.

The Hg…Hg and the Hg…C_α distances between adjacent molecules are such that both mercuriophilic and Hg-η^2-C_2 interactions appear to be contributing to the supramolecular aggregation process.

While the distances indicate that each of the individual interactions is relatively weak, it is the large number of them that will generate a significant driving force for aggregation.

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