

Syntheses and structures of highly hindered N-functionalised alkyl and amido group 12 complexes MR_2 ($M = Zn, Cd,$ and Hg), $[MRCl]_2$ ($M = Zn$ and Hg)

Tania R. van den Ancker^{a,*}, Lutz M. Engelhardt^b, Mark J. Henderson^b,
Geraldine E. Jacobsen^b, Colin L. Raston^b, Brian W. Skelton^b, Allan H. White^b

^a Department of Biological and Physical Sciences, University of Southern Queensland, Toowoomba, Qld. 4350, Australia

^b School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia

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Abstract

The reaction of MCl_2 ($M = Zn, Cd$ and Hg) with $Li(2-(C(SiMe_3)_2)(6-Me-C_5H_3N))$, $[Li(MeR)]$, affords mononuclear metal(II) alkyls. These, in the solid state, show intramolecular M–N interactions in their four-membered chelate rings, which progressively weaken down the series, the C–M–C angles becoming more open ($\langle M-N \rangle = 2.30(2), 2.52(2), 2.913(4)$ Å, C–M–C = $160.7(2), 168.5(2), 180(-)^\circ$). Alkylmercury chloride complexes have been prepared by the reaction of $HgCl_2$ with $[Li(MeR)]$, $Li(2-(C(SiMe_3)_2)(C_5H_4N))$, $[Li(HR)]$, or $Li(2-(NSiMe_3)(6-Me-C_5H_3N))$, $[Li(mps)]$, or from the redistribution reaction of the dialkyl (or amido) mercury complex with $HgCl_2$. The alkylmercury chloride complexes are dimeric or polymeric in nature with near-linear 2-coordination; ($Hg-Cl = 2.329(5), 2.318(4), 2.272(8)$ Å, $Cl-Hg-C(N) = 175.0(4), 174.7(4), 175.6(5)^\circ$). $Cd(2-(CH(SiMe_3))(6-Me-C_5H_3N))_2(tmen)$, prepared from the reaction of $Li(2-(CH(SiMe_3))(6-Me-C_5H_3N))$ and $CdCl_2$ in the presence of *tmen*, has also been structurally authenticated as the *rac* isomer with the *ipso* protons directed towards the *tmen*.

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1. Introduction

Bulky alkyl and aryl ligands have featured extensively in the development of novel main group chemistry where kinetic protection at the element in question is required, the most commonly used ligands being those devoid of β -hydrogen atoms. The main group chemistry of the ligands $2-(HC(SiMe_3)_2)(C_5H_4N)$, **1**, and $2-(HC(SiMe_3)_2)(6-Me-C_5H_3N)$, **2** (= *HMeR*), devoid of β -hydrogens, has been extensively investigated in the search for new classes of complexes [1]. The effect of the steric hindrance at the ligating C-centre, combined with the potential for stabilising N-donation to any metal(loid) centre, has resulted in the formation of mono-

meric, subvalent, hypervalent, electron deficient, low coordinate, and ionic species [1–6].

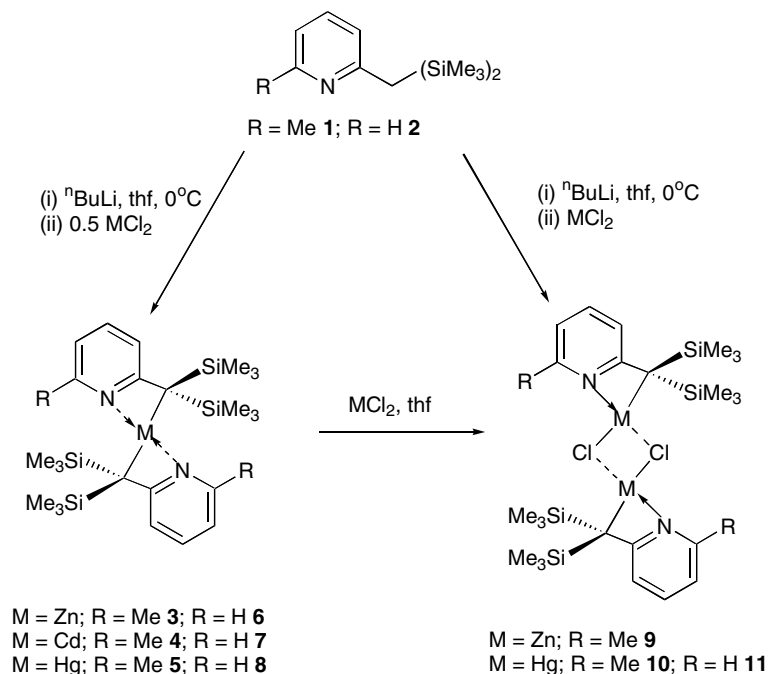
The synthesis and chemistry of group 12 alkyl and amido complexes has received considerable attention in recent years [7–12]. Herein, we report syntheses and structural studies of an array of functionalised pyridine complexes of zinc, cadmium and mercury based on a range of ligands with varying substitutions. The results presented show that the metal centres form four-coordinate, four-membered chelate ring systems which progressively weaken down the series culminating in no coordination through the pyridyl nitrogen for the heaviest congener.

2. Results and discussion

The group 12 dialkyl complexes $[M(MeR)_2]$, **3–5** (Scheme 1), were prepared as colorless crystals by the

* Corresponding author. Tel.: +61-7-4631-2363; fax: +61-7-4631-1530.

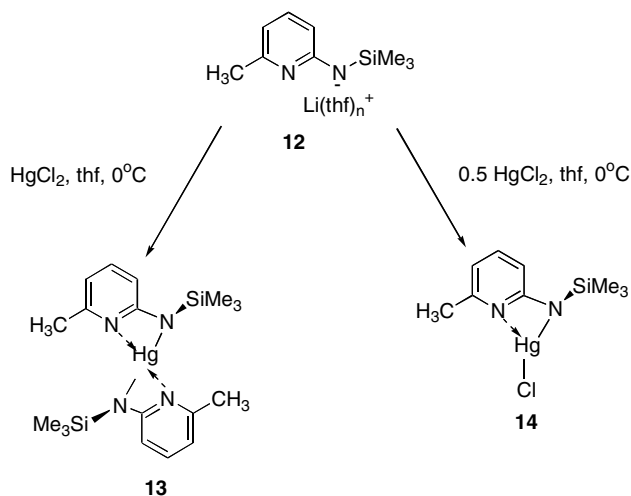
E-mail address: ancker@usq.edu.au (T.R. van den Ancker).



Scheme 1.

addition of solid anhydrous MCl_2 to a thf solution of $[\text{Li}(\text{MeR})]$ at room temperature. Similarly, the reaction of MCl_2 with $[\text{Li}(\text{HR})]$ afforded complexes $[\text{M}(\text{HR})_2]$, **6–8** [6]. The alkylmetal chlorides **9–11** were prepared via redistribution reactions of the corresponding dialkyl complexes, or by salt elimination for the zinc complex (Scheme 1). Redistribution was not an effective route for the preparation of **9** with equilibrium achieved at only 34% conversion (NMR spectroscopy).

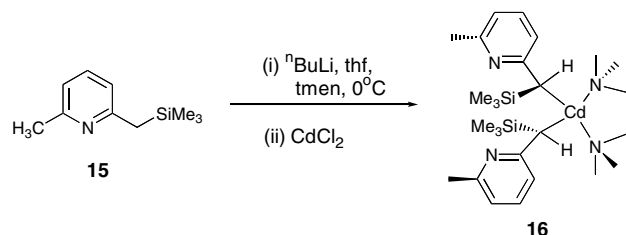
The analogous amido compounds **13**, **14** based on the related ligand 2-(NHSiMe_3)(6-Me- $\text{C}_5\text{H}_3\text{N}$), Hmpsa, were prepared similarly from the reaction of $\text{Li}(2\text{-(NHSiMe}_3\text{)}(6\text{-Me-}\text{C}_5\text{H}_3\text{N}))$, $[\text{Li}(\text{mpsa})]$, **12**, in thf with



Scheme 2.

HgCl_2 (Scheme 2). Attempts to prepare the corresponding Hg(I) amide complex by reaction of the lithium amide in thf with Hg_2Cl_2 were not successful, with the product disproportionating to Hg(0) and **13**. The corresponding zinc(II) amido complexes were prepared previously from the reactions of Hmpsa with ZnEt_2 or from $[\text{Li}(\text{mpsa})]$ and ZnCl_2 [7]. The less substituted complex of cadmium, $\text{Cd}(\text{HC}(\text{SiMe}_3)(6\text{-Me-}2\text{-}\text{C}_5\text{H}_3\text{N}))_2(\text{tmen})$, **16**, was prepared by salt elimination reaction between $\text{Li}(2\text{-(CH}(\text{SiMe}_3\text{)}(6\text{-Me-}\text{C}_5\text{H}_3\text{N})))$, $[\text{Li}(\text{MerH})]$, and CdCl_2 in the presence of tmen (Scheme 3).

Series of NMR data of 6-membered aromatic heterocycles including substituted pyridines have been compiled by Batterham [13] and Katrizky [14]. Changes in the electronegativity of the substituent result in only slight changes in the resonances of the pyridine ring protons and carbons. The ^1H NMR and ^{13}C NMR spectra of the above group 12 complexes are similar to those of the conjugate acids of the ligand. Slight perturbations of ca. 3 ppm are found in the ^{13}C NMR spectra, except for those of the α -carbon (C_7). The C_7



Scheme 3.

resonances of complexes **3–5** are found at 42–61 ppm, and the resonances of complexes **9** and **10** are further upfield at 28–29 ppm. The amido complexes **13** and **14** display virtually identical ^1H , ^{13}C and ^{29}Si NMR spectra and are typical of those obtained for metal complexes of the ligand [7,15,16].

In the solid state, adducts **3** and **4** are isomorphous, one molecule of complex comprising the asymmetric unit of each structure. Although the molecules are devoid of crystallographic symmetry, the two ligands are related by a *quasi*-2 axis passing between them (Fig. 1).

The C–M–C axes in the coordination spheres approach linearity, the angle increasing on passing from Zn to Cd, as might be expected on electronic grounds. Contrary to expectations arising out of the relaxation of any steric effects with increase in metal size, the M–C bonds are strengthened relative to the M–N, which are unexpectedly long in the Cd adduct. The dihedral angle between the two aromatic ligand planes is essentially similar in both adducts (Table 1).

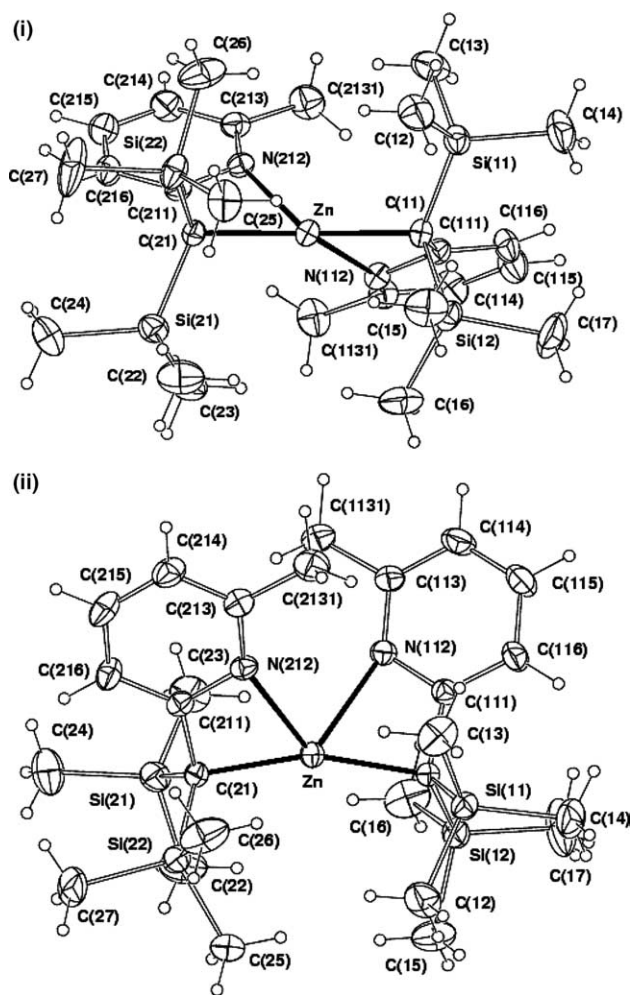


Fig. 1. Molecular structure of **3** (the Cd analogue **4** is isomorphous), (i) normal to, and (ii) down, its *quasi*-2 axis.

Some asymmetry (lattice forces?) is found between the two ligands in both complexes in respect of the metal atom out-of-plane deviations. The metal atom deviates appreciably more from the plane of ligand 1 than of ligand 2. This difference is barely reflected, if at all, in metal-ligand atom distances, the disparity in silicon atom deviations within each ligand, presumably coupled to the metal deviation, being more consistent.

In **16**, the structural form is different, the nitrogen atoms being supplanted by the introduction of a chelating pair from the tmen ligand, so that the organic ligand is now clearly unidentate. The metal environment, however, is remarkably similar, exact twofold crystallographic symmetry being found, with one-half of the molecule comprising the asymmetric unit (Fig. 2). The two coordination again dominates, evident in the short Cd–C distances, (2.217(7) Å) which are closely comparable with those in **4**. These are associated with a large C–Cd–C angle (152.5(2)°) (cf. 2.213(7), 2.220(6) Å, 168.5(2)°). This is diminished relative to that in **4**, despite the longer M–N distances, and associated with a larger (chelate) N–M–N angle, hinting at possible steric effects (Table 2).

Comparison of the above $[\text{M}(\text{MeR})_2]$, **3–5**, geometries with those of $[\text{M}(\text{HR})_2]$, **6–8**, previously reported only briefly [6], but presented more comprehensively and comparatively here in Table 1, is instructive, insofar as changes consequent primarily upon substitution or loss of the methyl substituent may be noted. The $[\text{M}(\text{HR})_2]$ arrays are isomorphous with each other and inclusive of $\text{M} = \text{Mg}$, but with two molecules in the asymmetric unit of the structure. Although more comprehensive, this series has the difficulty of greater crystallographic intractability with consequent somewhat lower precision in the determinations. In respect of metal atom environments, it is of interest to note that, whereas M–N distances are closely comparable for $[\text{M}(\text{HR})_2]/[\text{M}(\text{MeR})_2]$ for common $\text{M} = \text{Zn}$ or Cd, M–C are appreciably shorter in **4**. This is a rather surprising result, perhaps, since the 2-($-\text{C}(\text{SiMe}_3)_2(6\text{-Me-C}_5\text{H}_3\text{N})$) adduct might be expected to be more subject to steric crowding and strain. Within the $[\text{M}(\text{MeR})_2]$ array, it is of interest to note that, whereas M–N increase monotonically with increase in atomic number, M–C do not, Zn–C offering the shortest distances of the series. This parallels a trend which sees the difference [(M–N)–(M–C)] become increasingly and monotonically positive from a value initially negative at $\text{M} = \text{Mg}$ in the **6–8** array. Similarly, in both series of complexes, the largest angles in all coordination spheres are C–M–C, becoming increasingly linear with increasing atomic number. In the $[\text{M}(\text{HR})_2]$ series, in parallel, N–M–N diminish, but for the two members of the $[\text{M}(\text{MeR})_2]$ array, N–M–N are essentially constant. Perhaps the most interesting consequence of the effect of the addition of the methyl substituents in $[\text{M}(\text{MeR})_2]$ cf. $[\text{M}(\text{HR})_2]$ is the very

Table 1
Selected bond lengths and angles in complexes Mg(HR)₂, **3**, **4**, **6** and **7**

Compound (M)	Mg(HR) ₂	3 (Zn)	4 (Cd)	6 (Hg)	7 (Cd)
<i>Bond lengths (Å)</i>					
M–C(11)	2.217(8), 2.220(10)	2.04(2), 2.06(2)	2.26(3), 2.29(2)	2.054(4)	2.213(7)
M–C(21)	2.224(9), 2.214(11)	2.10(2), 2.07(2)	2.27(3), 2.28(2)	2.057(4)	2.220(6)
M–N(112)	2.141(8), 2.131(9)	2.33(2), 2.29(2)	2.52(2), 2.50(2)	2.315(4)	2.534(6)
M–N(212)	2.126(7), 2.128(7)	2.29(2), 2.26(2)	2.49(2), 2.49(2)	2.289(4)	2.499(6)
<i>Bond angles (°)</i>					
C(11)–M–C(21)	158.9(4), 155.3(4)	165.5(6), 163.4(6)	175.5(6), 173.1(6)	160.7(2)	168.5(2)
N(12)–M–N(22)	118.4(3), 116.5(3)	107.4(6), 107.9(6)	110.9(6), 109.0(6)	86.7(1)	86.1(2)
C(11)–M–N(112)	67.4(3), 67.5(4)	67.1(7), 66.8(7)	58.5(6), 59.8(7)	66.3(21)	60.7(2)
C(21)–M–N(212)	67.0(3), 67.3(3)	67.3(6), 66.7(7)	59.8(7), 59.8(6)	66.3(2)	60.9(2)
C(11)–M–N(212)	125.2(3), 128.1(4)	123.0(6), 125.6(7)	123.5(7), 124.7(7)	128.8(2)	127.6(2)
C(21)–M–N(112)	125.0(3), 126.9(4)	121.9(7), 123.1(7)	124.2(6), 125.2(7)	131.4(2)	130.4(2)
M–C(11)–C(111)	84.5(5), 84.6(6)	91(3), 92(1)	96(2), 96(1)	92.0(2)	95.4(4)
M–C(21)–C(211)	84.5(6), 84.8(6)	91(1), 91(1)	91(1), 94(2)	92.7(3)	95.8(4)
M–N(112)–C(111)	90.6(6), 90.9(6)	85(1), 88(1)	84(1), 88(1)	85.7(3)	86.4(4)
M–N(212)–C(211)	91.7(5), 91.5(5)	88(1), 89(1)	85(2), 86(1)	87.1(3)	88.5(4)
C(11)–C(111)–N(112)	116.8(9), 116.9(9)	118(2), 113(2)	120(2), 117(2)	113.7(4)	115.8(6)
C(21)–C(211)–N(112)	116.2(8), 115.9(8)	114(2), 113(2)	124(2), 120(2)	113.5(4)	114.6(6)
M–C(11)–Si(11)	112.5(4), 111.8(7)	109(1), 109(1)	103(1), 107(1)	112.8(2)	108.9(3)
M–C(21)–Si(21)	110.4(4), 110.8(4)	112(1), 112(1)	105(1), 106(1)	112.8(2)	108.9(3)
M–C(11)–Si(12)	112.8(4), 109.7(7)	113(1), 112(1)	108(1), 106(1)	110.6(2)	108.0(3)
M–C(21)–Si(22)	114.5(5), 114.8(4)	110(1), 111(1)	104(1), 105(1)	108.5(2)	106.6(3)
C(111)–C(11)–Si(12)	112.3(6), 109.7(7)	115(1), 112(1)	120(1), 113(1)	107.6(3)	108.8(5)
C(211)–C(21)–Si(21)	111.8(7), 109.8(6)	112(1), 111(1)	112(1), 116(1)	115.2(3)	114.6(5)
C(111)–C(11)–Si(11)	110.9(6), 111.8(7)	107(1), 108(1)	110(1), 114(1)	114.4(3)	115.2(5)
C(211)–C(21)–Si(22)	109.7(7), 114.2(6)	109(1), 109(1)	118(1), 113(1)	108.4(3)	109.6(4)
Si(11)–C(11)–Si(12)	118.9(4), 120.2(5)	118(1), 120(1)	116(1), 121(1)	116.7(2)	118.0(4)
Si(21)–C(21)–Si(22)	118.4(5), 117.8(8)	120(1), 119(1)	121(1), 118(1)	116.5(2)	118.6(3)
<i>Atom deviations (Å) from the C₅N plane</i>					
δM	0.26(1), 0.11(1)	0.13(3), 0.04(1)	0.27(4), 0.03(4)	0.542(7)	0.55(1)
δM'	–0.18(1), –0.21(1)	–0.07(3), –0.12(3)	–0.06(4), –0.09(4)	0.196(7)	0.10(1)
δSi(11)	1.48(1), 1.51(2)	1.49(4), 1.56(5)	1.58(4), 1.51(5)	1.311(9)	1.38(1)
δSi(21)	1.81(1), 1.74(1)	1.72(4), 1.72(3)	1.69(4), 1.61(4)	1.404(8)	1.49(1)
δSi(12)	–1.66(1), –1.66(2)	–1.69(4), –1.65(4)	–1.61(4), –1.72(5)	–1.740(8)	–1.71(1)
δSi(22)	–1.30(1), –1.37(1)	–1.45(4), –1.46(4)	–1.52(5), –1.59(5)	–1.734(7)	–1.79(1)
<i>Plane 1 plane 2 interplanar dihedral angles (°)</i>					
	85.9(3), 89.5(3)	88.5(8), 89.5(9)	89.4(9), 89.5(10)	48.9(2)	47.6(3)

The two values for the isomorphous Mg(HR)₂, **3** and **4** are for the two molecules of the asymmetric unit.

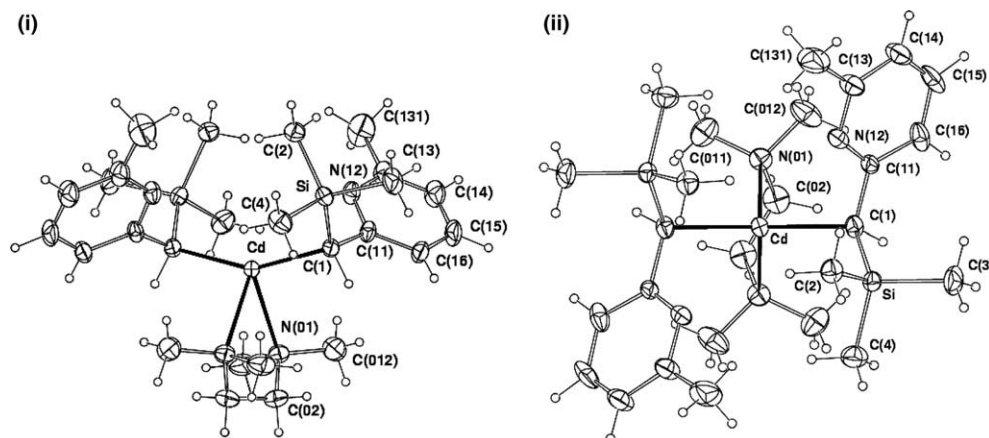


Fig. 2. Molecular structure of **16**, (i) normal to, and (ii) down, its 2 axis.

Table 2
[Cd(MerH)₂(tmen)], **16**: selected geometries (primed atoms are generated by the intramolecular twofold axis)

Bond lengths (Å)			
Cd–C(1)	2.217(7)	Cd–N(01)	2.606(5)
Bond angles (°)			
C(1)–Cd–C(1')	152.5(2)	N(01)–Cd–N(01')	72.3(2)
C(1)–Cd–N(01)	100.5(2)	C(1)–Cd–N(01')	101.7(2)
Cd–C(1)–Si	112.3(3)	Cd–C(1)–C(11)	107.1(5)
Si–C(1)–C(11)	113.7(4)		
Atom deviations (Å) from the C ₅ N plane			
δCd	–1.52(1)	δSi	1.73(1)
Torsion angles (°)			
Cd–N(01)–C(02)	46.7(8)	Cd–C(1)–C(11)	54.3(7)
–C(02')		–N(12)	
C(011)–N(01)–C(02)	–74.6(8)	C(012)–N(01)	165.1(7)
–C(02')		–C(02)–C(02')	
N(01)–C(02)–C(02')	–69.9(10)		
–N(01')			

considerable change in relative pitch of the two C₅N aromatic ligand planes, the interplanar dihedral angles being almost/essentially 90° for **6–8**, but around 48° for **3** and **4**. Out-of-plane deviations of the metal atoms from the C₅N planes are greater for [M(MeR)₂] cf. [M(HR)₂], suggestive of increased strain. In **5**, one-half of the molecule comprises the asymmetric unit of the structure again, the metal atom this time being located on an inversion centre, and the mercury atom being linearly two-coordinated by the two carbon atoms of the ligands, Hg–C 2.156(3) Å. C(11) is effectively tetrahedral; Si–C–Si is large (118.6(2)°), but the remaining angles range between 103.8(2) and 111.1(3)°. Hg–N is 2.913(4) Å (Fig. 3). The mercury atom is almost coplanar with the ligand plane (deviation 0.16(1) Å), with the

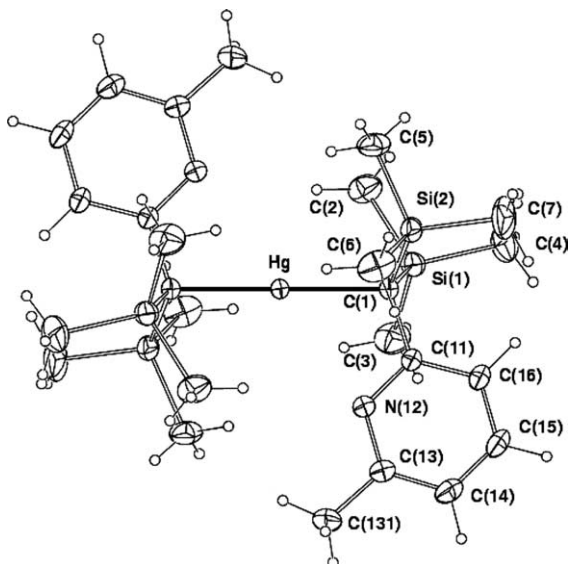


Fig. 3. Molecular structure of **5** normal to the C–Hg–C line.

silicon atoms equally disposed to either side (1.64(1), –1.60(1) Å). In these respects, the [M(MeR)₂] core environment resembles that of [M(HR)₂] much more nearly than in the lighter atom analogues. This is presumably contingent on increased metal atom size and linear co-ordination about the metal. **8** is devoid of crystallographic symmetry, with Hg–C 2.155(7), 2.157(8) Å, C–Hg–C 179.5(3)° and Hg–N 2.771(7), 2.794(7) Å, rather shorter than in **5**.

The determinations for the remaining structures presented are somewhat inferior, being of oligo/polymeric species offering poor quality material. The structure of **10** is supported by the determination for the unmethylated pyridine analogue **11** which is isomorphous but with one of the acute triclinic angles having become obtuse. Here, one molecule comprises the asymmetric unit of each structure (Fig. 4). For the two compounds, respectively, Hg–Cl are 2.329(4), 2.317(4) Å, Hg–C 2.12(1), 2.12(1) Å, Cl–Hg–C 174.9(3), 174.5(4)°; Hg...N are 2.79(1), 2.76(1) Å. The angles at the coordinated carbon range between 103.3(5)–107.9(5), 102.6(6)–109.1(10)°, with two outliers: C(1)–C(0)–Si(1) 116.6(9), 114(1); Si(1)–C(0)–Si(2) 116.4(7), 119.1(7)°. Hg lies 0.52(3), 0.33(3) Å out of the C₅N plane, Si(1) 1.11(3), 1.30(3); Si(2) –1.90(2), –1.86(3) Å to either side. Incipient dimer formation is found through the interactions of inversion related pairs of molecules by way of Hg...Cl approaches at 3.559(6), 3.585(5) Å. Hg...Hg being 4.749(1), 4.798(1) Å.

An interesting comparison is possible here with the structure of the amide analogue, **14** (Fig. 5). Here the contrast in bonding sites evinced in the 'MeR' complexes persists, Hg–N (amide) being 2.04(2) Å. However Hg–N(py) is now much shorter at 2.36(2) Å; N(amide)–Hg–Cl is 175.8(6)°, with Hg–Cl 2.275(9) Å and Hg coplanar with the C₅N array (0.004(4) Å).

Intermolecular approaches here result in the formation of a polymer of dimers; the molecule of the asymmetric unit is approached in quasi-parallel fashion by

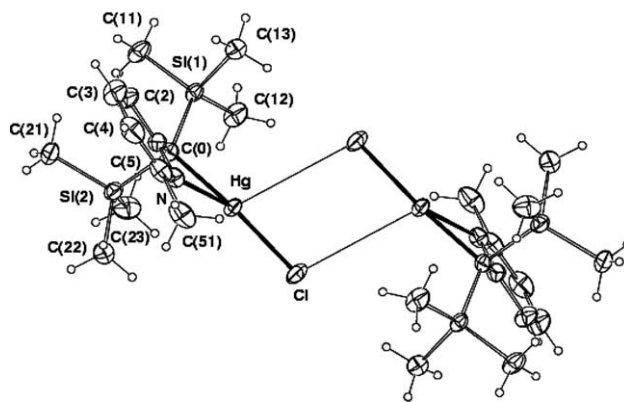


Fig. 4. Molecular structure of **10** showing the incipient dimer formation.

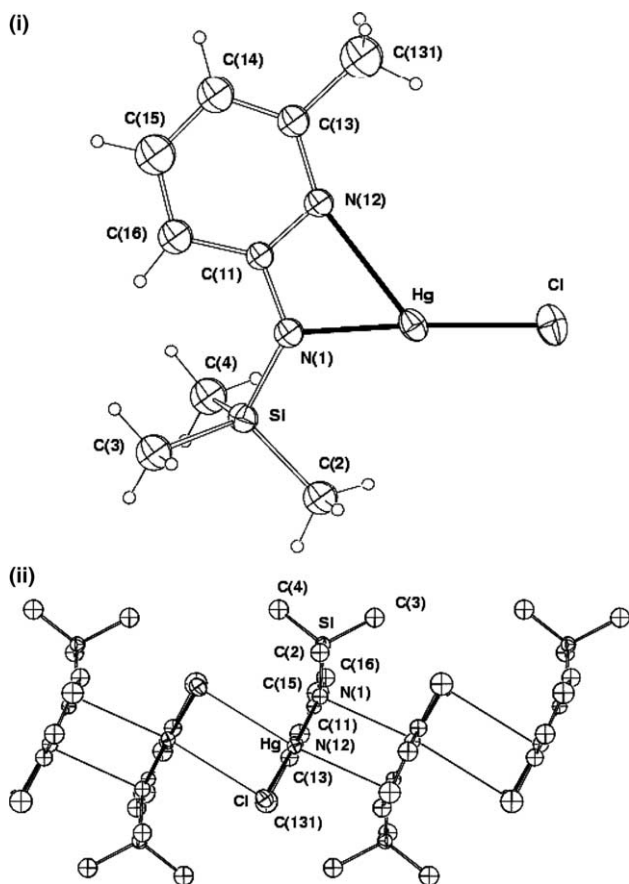


Fig. 5. Molecular structure of **14**, (i) normal to the ligand plane, and (ii) showing the incipient polymer formation.

another molecule at $(11/2 - x, 11/2 - y, 11/2 - z)$ (Hg...N(1), Cl 3.23(2), 3.28(2) Å), and, less intimately, on the other side by the molecule at $(1 - x, y, 11/2 - z)$ (Hg...Cl 3.722(7) Å), Hg...Hg being 4.063(3), 3.888(4) Å, respectively.

3. Experimental

3.1. General

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried then freeze–thaw–degassed prior to use. ZnCl₂, CdCl₂ and HgCl₂ were purchased from Aldrich and used without purification, tmen was also purchased from Aldrich and purified by distillation prior to use. ⁿBuLi was obtained from Metallgesellschaft (AG) Germany, as a 1.60 M solution in hexane and was standardised prior to use. **1** [3], **2** [3], **12** [16], and **15** [17] were prepared by literature procedures. ¹H NMR were recorded on a Hitachi–Perkin–Elmer R-24B, Bruker WP-80, or a Varian Gemini 200 spectrometer in deuterated chloro-

form or benzene and referenced to the residual ¹H resonances of the solvent (δ 7.24 and 7.15, respectively). ¹³C NMR were recorded on a Bruker WP-80 or a Varian Gemini 200 spectrometer using broad band proton decoupling and referenced to the ¹³C resonances of the deuterated solvent (δ 77.0 and 128.0, respectively). ²⁹Si NMR were run on a Bruker WM 300 spectrometer and were referenced to tetramethylsilane (δ 0.00) externally. Elemental analyses were carried out by the Canadian Microanalytical Services Ltd., Vancouver, Canada or Micro Analytical Services Pty. Ltd., Melbourne, Australia. Melting points were determined in sealed glass capillaries under argon and are uncorrected.

3.2. Preparation of [Zn(2-(C(SiMe₃)₂)(6-Me-C₅H₃N))₂] (**3**)

ⁿBuLi (2.65 cm³, 4.1 mmol) was added slowly to an ice-cooled solution of **1** (1.0 g, 3.98 mmol) in thf (25 cm³). After stirring the resultant solution for 10 min, ZnCl₂ (0.27 g, 1.98 mmol) was added over 10 min. The mixture was stirred at room temperature overnight, volatiles were removed in vacuo, the resulting solid was extracted into hexane, the extract filtered and the filtrate cooled to -30 °C, affording colorless crystals (0.95 g, 85%), m.p. 135 °C (Found: C, 54.74; H, 8.62; N, 5.31 C₂₆H₄₈N₂Si₄Zn requires C, 55.13; H, 8.54; N, 4.95); δ_{H} (200 MHz, C₆D₆) 0.37 (18H, s, Si(CH₃)₃), 1.69 (3H, s, CH₃), 6.33 (1H, m, Ar H), 7.01 (1H, m, Ar H), 6.98 (1H, m, Ar H); δ_{C} (50.3 MHz, C₆D₆) 3.5 (Si(CH₃)₃), 22.7 (CH₃), 41.8 (C(SiMe₃)₂), 117.8, 121.1, 137.4, 156.1, 172.1 (C₅H₃N).

3.3. Preparation of [Cd(2-(C(SiMe₃)₂)(6-Me-C₅H₃N))₂] (**4**)

This preparation follows that of **3** using **1** (0.6 g, 2.39 mmol), ⁿBuLi (1.55 cm³, 2.5 mmol) and CdCl₂ (0.22 g, 1.2 mmol), **4** being obtained as colorless crystals (0.63 g, 85%), mp 130 °C (Found: C, 49.78; H, 7.88; N, 4.92. C₂₆H₄₈N₂Si₄Cd requires C, 50.91; H, 7.89; N, 4.57); δ_{H} (200 MHz, C₆D₆) 0.34 (18H, s, Si(CH₃)₃), 1.96 (3H, s, CH₃), 6.43 (1H, m, Ar H), 7.05 (1H, m, Ar H), 6.99 (1H, m, Ar H); δ_{C} (50.3 MHz, C₆D₆) 3.5 (Si(CH₃)₃), 23.6 (CH₃), 49.0 (C(SiMe₃)₂), 118.0, 121.6, 137.0, 156.3, 165.5 (C₅H₃N).

3.4. Preparation of [Hg(2-(C(SiMe₃)₂)(6-Me-C₅H₃N))₂] (**5**)

This preparation follows that of **3** using **1** (0.2 g, 0.80 mmol), ⁿBuLi (0.6 cm³, 0.9 mmol) and HgCl₂ (0.11 g, 0.4 mmol), **5** being obtained as colorless crystals (0.11 g, 40%), m.p. 154 °C (Found: C, 44.54; H, 6.75; N, 3.92. C₂₆H₄₈N₂Si₄Hg requires C, 44.51; H, 6.89; N, 3.99); δ_{H} (200 MHz, CDCl₃) 0.14 (18H, s, Si(CH₃)₃), 2.26 (3H, s,

CH₃), 6.79 (2H, m, Ar H), 7.36 (1H, m, Ar H); δ_C (50.3 MHz, CDCl₃) 2.6 (Si(CH₃)₃), 24.3 (CH₃), 60.7 (C(SiMe₃)₂), 117.7, 121.6, 135.0, 156.3, 166.8 (C₅H₃N).

3.5. Preparation of [Zn(2-(C(SiMe₃)₂)(6-Me-C₅H₃N))-Cl] (**9**)

3.5.1. Method 1

This preparation follows that of **3** using **1** (1.0 g, 3.98 mmol), ⁿBuLi (2.65 mL, 4.1 mmol) and ZnCl₂ (0.65 g, 4.77 mmol), **9** being obtained as colorless crystals (0.9 g, 65%), m.p. 160 °C (Found: C, 44.24; H, 7.40; N, 5.22. C₁₃H₂₄NSi₂ClZn requires C, 44.44; H, 6.89; N, 3.99); δ_H (200 MHz, C₆D₆) 0.18 (18H, s, Si(CH₃)₃), 2.36 (3H, s, CH₃), 6.48 (1H, m, Ar H), 7.10 (1H, m, Ar H), 7.06 (1H, m, Ar H). δ_C (50.3 MHz, C₆D₆) 1.15 (Si(CH₃)₃), 24.4 (CH₃), 28.0 (C(SiMe₃)₂), 117.3, 119.7, 135.6, 157.1, 163.6 (C₅H₃N).

3.5.2. Method 2

A solution of **3** (0.54 g, 0.96 mmol) in thf (15 mL) was added dropwise to a thf (15 mL) solution of ZnCl₂ (0.121 g, 0.45 mmol) over 40 min at room temperature. The mixture was stirred for 1 week. Volatiles were then removed in vacuo and the white solid extracted into hexane. The mixture was filtered and the filtrate concentrated and cooled to -30 °C affording a colorless crystalline solid (0.23 g, 34% NMR).

3.6. Preparation of [Hg(2-(C(SiMe₃)₂)(6-Me-C₅H₃N))-Cl] (**10**)

This preparation follows that of **9** (Method 2) using **5** (0.0657 g, 0.094 mmol) and HgCl₂ (0.0256 g, 0.095 mmol), **10** being obtained as colorless needles (0.045 g, 100%), m.p. 154 °C (Found: C, 32.18; H, 5.07; N, 2.58. C₁₃H₂₄NSi₂ClHg requires C, 32.09; H, 4.97; N, 2.88); δ_H (200 MHz, CDCl₃) 0.08 (9H, s, Si(CH₃)₃), 0.14 (9H, s, Si(CH₃)₃), 6.70 (1H, m, Ar H), 6.87 (1H, m, Ar H), 7.43 (1H, m, Ar H); δ_C (50.3 MHz, CDCl₃) 1.1 (Si(CH₃)₃), 2.2 (Si(CH₃)₃), 24.5 (CH₃), 29.1 (C(SiMe₃)₂), 118.2, 119.7, 136.9, 157.1, 163.7 (C₅H₃N).

3.7. Preparation of [Hg(2-(C(SiMe₃)₂)(C₅H₄N))Cl] (**11**)

3.7.1. Method 1

This preparation follows that of **9** using **2** (0.3 g, 1.27 mmol), ⁿBuLi (0.75 cm³, 1.27 mmol) and HgCl₂ (0.34 g, 1.27 mmol), **11** being obtained as colorless crystals (0.09 g, 17%), m.p. 118 °C.

3.7.2. Method 2

This preparation follows that of **9** using **8** (0.3 g, 0.45 mmol) and HgCl₂ (0.121 g, 0.45 mmol), **11** being obtained as colorless crystals (0.4 g, 95%), m.p. 118–120 °C

(Found: C, 30.4; H, 4.65; N, 2.95; Cl, 7.59. C₁₂H₂₂NSi₂ClHg requires C, 30.5; H, 4.66; N, 2.97; Cl, 7.52); δ_H (60 MHz, CDCl₃) 0.75 (18H, s, Si(CH₃)₃), 7.65 (2H, m, Ar H), 8.05 (1H, m, Ar H), 8.95 (1H, m, Ar H); δ_C (20.1 MHz, CDCl₃) 2.1 (Si(CH₃)₃), 68.1 (C(SiMe₃)₂), 120.2, 121.4, 136.3, 148.1, 164.6 (C₅H₄N).

3.8. Preparation of [Hg(2-N(SiMe₃)(6-Me-C₅H₃N))₂] (**13**)

A solution of **12** (0.50 g, 2.65 mmol) in thf (10 cm³) was added slowly to a slurry of HgCl₂ (0.72 g, 2.65 mmol) in thf (15 cm³) at 0 °C, and stirred at room temperature for 2 h. Volatiles were removed in vacuo, and the resulting solid was extracted into hexane (3 × 30 cm³). The extract was filtered and volatiles were removed in vacuo. The resulting solid was washed with pentane (10 cm³), affording a colorless microcrystalline solid (1.35 g, 91%), m.p. 88–96 °C dec (Found: C, 39.80; H, 5.68; N, 10.01. C₁₈H₃₀N₄Si₂Hg requires C, 38.66; H, 5.40; N, 10.01); δ_H (80 MHz, C₆D₆) 0.34 (9H, s, Si(CH₃)₃), 2.22 (3H, s, CH₃), 6.3–7.2 (3H, m, Ar H); δ_C (20.1 MHz, C₆D₆) 1.2 (Si(CH₃)₃), 24.1 (CH₃), 107.4, 112.2, 138.2, 156.3, 163.2 (C₅H₃N). δ_{Si} (59.63 MHz, C₆D₆) 4.05 (SiMe₃).

3.9. Preparation of [Hg(2-N(SiMe₃)(6-Me-C₅H₃N))Cl] (**14**)

A solution of **12** (0.86 g, 4.60 mmol) in thf (10 cm³) was added slowly to a slurry of HgCl₂ (1.28 g, 4.71 mmol) in thf (10 cm³) at 0 °C, and stirred at room temperature for 20 h. Volatiles were removed in vacuo, and the resulting solid sublimed (85–100 °C, 0.1 mmHg) affording colorless crystals (0.9 g, 50%), m.p. 90–98 °C dec; δ_H (80 MHz, C₆D₆) 0.28 (9H, s, Si(CH₃)₃), 2.18 (3H, s, CH₃), 6.2–7.2 (3H, m, Ar H); δ_C (20.1 MHz, C₆D₆) 1.2 (Si(CH₃)₃), 24.0 (CH₃), 107.2, 112.3, 156.2, 162.9 (C₅H₃N); δ_{Si} (59.63 MHz, C₆D₆) 4.07 (SiMe₃).

3.10. Preparation of [Cd(2-(CH(SiMe₃))(6-Me-C₅H₃N))₂(tmen)] (**16**)

To a solution of **1** (1.34 g, 7.5 mmol) in thf (30 mL) and tmen (0.9 g, 7.5 mmol) was added ⁿBuLi (5.5 mL, 7.7 mmol) at 0 °C, and the mixture was stirred for 10 min. To this solution was slowly added CdCl₂ (0.7 g, 3.82 mmol) over 15 min giving a green solution. Volatiles were removed in vacuo and the resulting green oil was extracted with hexane and the mixture filtered. Concentration and cooling of the filtrate to -30 °C gave a green crystalline product over 2 weeks (1.77 g, 77%), m.p. 95 °C dec; δ_H (200 MHz, C₆D₆) 0.07 (18H, s, Si(CH₃)₃), 2.13 (12H, s, NCH₃), 2.32 (4H, s, NCH₂), 2.36 (2H, s, CHSiMe₃), 2.43 (6H, s, CH₃), 6.55 (4H, m, Ar H), 7.05 (2H, m, Ar H); δ_C (50.3 MHz, C₆D₆) -1.4

(Si(CH₃)₃), 30.2 (CH₃), 46.1 (NCH₃), 58.5 (NCH₂), 64.3 (CHSiMe₃), 118.6, 119.2, 135.9, 156.0, 169.3 (C₅H₃N).

4. X-ray crystallography

4.1. General

Unique room-temperature single counter data sets were measured on capillary mounted specimens ($2\theta/\theta$ scan mode; monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; T ca 295 K). N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered “observed” and used in the full matrix least squares refinements after gaussian absorption correction. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being constrained at estimated values. Conventional residuals on $|F|$, R, R_w are quoted at convergence, statistical weights derivative of $\sigma^2(I) = (\sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff}))$ being employed. Neutral atom complex scattering factors were employed, computation using the Xtal 3.2 program system [18]. Pertinent results are given below and in the figures and tables and deposition. Individual variations in procedure/abnormalities/idiosyncrasies are noted below as “*variata*”.

4.2. Crystal and refinement data

4.2.1. Compounds 3 and 4

M(MeR)₂, M = Zn, Cd \equiv C₂₆H₄₈N₂Si₄M. Monoclinic, space group $P2_1/c$ (C_{2h}⁵, No. 14), $Z = 4$.

(i) M = Zn, $M_r = 566.4$. $a = 16.112(7)$, $b = 10.593(3)$, $c = 19.365(12)$ Å, $\beta = 90.53(4)^\circ$, $V = 3305$ Å³. $D_c = 1.138$ g cm⁻³. $\mu_{Mo} = 9.0$ cm⁻¹; specimen: $0.35 \times 0.42 \times 0.37$ mm; $A_{min\ max}^* = 1.28, 1.38$. $2\theta_{max} = 50^\circ$; $N = 5801$, $N_o = 3261$; $R = 0.043$, $R_w = 0.041$.

(ii) M = Cd, $M_r = 613.4$. $a = 16.377(11)$, $b = 10.607(2)$, $c = 19.485(14)$ Å, $\beta = 91.69(5)^\circ$, $V = 3383$ Å³. $D_c = 1.204$ g cm⁻³. $\mu_{Mo} = 8.0$ cm⁻¹; specimen: $0.32 \times 0.42 \times 0.38$ mm; $A_{min\ max}^* = 1.25, 1.29$. $2\theta_{max} = 50^\circ$; $N = 5398$, $N_o = 3236$; $R = 0.044$, $R_w = 0.047$.

4.2.2. Compound 5

Hg(MeR)₂ \equiv C₂₆H₄₈HgSi₄N₂, $M_r = 701.6$. Triclinic, space group $P\bar{1}$ (C₁¹, No. 2), $a = 10.494(8)$, $b = 10.432(7)$, $c = 8.979(4)$ Å, $\alpha = 114.63(5)^\circ$, $\beta = 90.47(5)^\circ$, $\gamma = 108.07(6)^\circ$, $V = 839$ Å³. $D_c(Z = 1) = 1.389$ g cm⁻³. $\mu_{Mo} = 48$ cm⁻¹; specimen: $0.55 \times 0.23 \times 0.42$ mm; $A_{min\ max}^* = 2.7, 6.5$ (analytical correction). $2\theta_{max} = 60^\circ$; $N = 4884$, $N_o = 4828$; $R = 0.032$, $R_w = 0.039$.

4.2.3. Compound 16

Cd(MerH)₂(tmen) \equiv C₂₆H₄₈CdN₄Si₂, $M_r = 585.3$. Monoclinic, space group $C2/c$ (C_{2h}⁶, No. 15), $a = 18.373(2)$, $b = 9.900(4)$, $c = 18.540(8)$ Å, $\beta = 109.55(3)^\circ$,

$V = 3178$ Å³. $D_c(Z = 4) = 1.223$ g cm⁻³. $\mu_{Mo} = 7.8$ cm⁻¹; specimen: $0.25 \times 0.42 \times 0.35$ mm; $A_{min\ max}^* = 1.19, 1.38$. $2\theta_{max} = 55^\circ$; $N = 2764$, $N_o = 2317$; $R = 0.052$, $R_w = 0.062$.

4.2.4. Compounds 10 and 11

HgXCl, X = MeR⁻, R⁻, triclinic, space group $P\bar{1}$, $Z = 2$.

(i) Hg(MeR)Cl \equiv C₁₃H₂₄ClHgNSi₂, $M_r = 486.6$. $a = 10.722(4)$, $b = 9.859(1)$, $c = 8.749(1)$ Å, $\alpha = 87.49(1)^\circ$, $\beta = 87.03(3)^\circ$, $\gamma = 91.38(2)^\circ$, $V = 922.4$ Å³. $D_c = 1.752$ g cm⁻¹. $\mu_{Mo} = 83$ cm⁻¹. Absorption correction: not recorded. $2\theta_{max} = 60^\circ$; $N = 4290$ (refinement on F^2 , all data $I > 2\sigma(I)$, SHELX program system [19]), $R1 = 0.079$, $wR2 = 0.19$.

(ii) Hg(HR)Cl \equiv C₁₂H₂₂NCIHgSi₂, $M_r = 472.5$. $a = 10.168(3)$, $b = 9.765(3)$, $c = 8.837(3)$ Å, $\alpha = 87.83(2)^\circ$, $\beta = 86.52(2)^\circ$, $\gamma = 86.83(2)^\circ$, $V = 873.9$ Å³. $D_c = 1.795$ g cm⁻¹. $\mu_{Mo} = 94$ cm⁻¹; specimen: $0.48 \times 0.30 \times 0.10$ mm; $A_{min\ max}^* = 0.24, 0.40$. $2\theta_{max} = 50^\circ$; $N = 2482$, $N_o = 2152$; $R = 0.054$, $R_w = 0.064$.

4.2.5. Compound 14

Hg(mpsa)Cl \equiv C₉H₁₅ClHgN₂Si, $M_r = 415.4$. Monoclinic, space group $I2/c$ (C_{2h}⁶, No. 15(variant)), $a = 15.099(14)$, $b = 9.781(2)$, $c = 18.083(10)$ Å, $\beta = 102.38(5)^\circ$, $V = 2608$ Å³. $D_c(Z = 8) = 2.115$ g cm⁻³. $\mu_{Mo} = 118$ cm⁻¹; specimen: $0.45 \times 0.11 \times 0.15$ mm; $A_{min\ max}^* = 2.4, 4.5$ (analytical correction). $2\theta_{max} = 45^\circ$; $N = 2096$, $N_o = 1238$; $R = 0.069$, $R_w = 0.074$.

Variata. The crystal decomposed by ca. 20% during data collection; data were measured on a single component of a twinned crystal. Weak and limited data would support refinement of anisotropic displacement parameter forms for Hg, Cl, Si only.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 215162–215168 for compounds **3**, **4**, **5**, **10**, **11**, **14** and **16**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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