Heteroatom Chemistry
Volume 9, Number 4, 1998

Crystal and Molecular Structure of $[Hg_3(H_2pdm)_2(Hpdm)\ (\mu\text{-}Cl)_2Cl_3]$

Norberto Farfán[1] and Herbert Höpfl[2]

[1]Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apdo. Postal 14-740, 07000 México, D.F., México; Fax: Int. code + (5) 747 71 13; E-mail: jfarfan@mail.cinvestav.mx

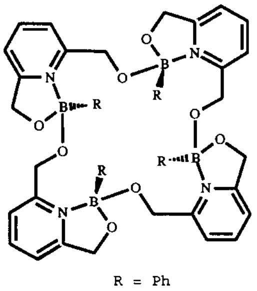
[2]Departmento de Química, Universidad Autónoma del Estado de Morelos, Avenida Universidad No. 1001, Col. Chamilpa, 62210 Cuernavaca, Morelos, México

Received 1 August 1997; revised 1 December 1997

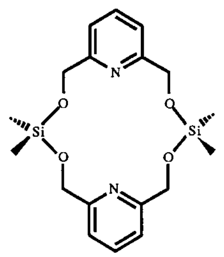
ABSTRACT: *The reaction between mercury(II)-chloride and 2,6-pyridinedimethanol provides a molecule with the empirical formula* $[Hg_3(H_2pdm)_2(Hpdm)\ (\mu\text{-}Cl)_2Cl_3]$*, whose crystal and molecular structure has been studied:* $a = 10.640(1)$, $b = 10.818(2)$, $c = 13.159(2)$ Å, $\alpha = 88.480(5)$, $\beta = 75.067(4)$, $\gamma = 89.736(5)°$, $V = 1463.0(4)$ Å^3, $Z = 2$, *P-1. The molecule consists of a central [Hg(Hpdm)Cl] fragment that is connected by chloro bridges to two lateral fragments of identical constitution,* $[Hg(H_2pdm)Cl_2]$*. The coordination geometry around the central mercury atom is distorted octahedral, while the lateral metal atoms are located in significantly different, distorted square-pyramidal polyhedrons. The tridentate ligand induces the formation of the square-pyramidal environment instead of the trigonal-bipyramidal one that is normally preferred by* d^{10} *systems.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:377–382, 1998

INTRODUCTION

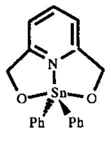
We are interested in the thermodynamic stability of the coordinative N→B bond in diphenyl(2-pyridylmethoxy-*O,N*)- and diphenyl(2-pyridylcarbonyloxy-*O,N*)boranes [1–3]. A synthesis involving 2,6-pyridinedimethanol (H_2pdm) and phenylboronic acid leads to the formation of a very stable tetrameric boronate (**1**), in which the tridentate chelating ligand is connected to two different boron atoms, forming only one five-membered heterocycle with the phenylboryl moiety [4]. With dichlorodimethylsilane, a dimeric macrocycle (**2**) showing no coordinative N→Si bond is obtained [5], while the bulkier tin atom gives a monomeric structure (**3**) [6].



1



2



3

As a starting point in the study of the coordination behavior of 2,6-pyridinedimethanol with other metal atoms or organometallic moieties, this diol has been reacted with $HgCl_2$. Common coordination numbers for mercury(II) range from 2 up to 8 [7,8] due to the closed d-shell of Hg(II), so that each of the above-mentioned structure types 1–3 could be a

---

Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his seventieth birthday.

Correspondence to: Norberto Farfán.

possible product. The present contribution shows that mercury(II) prefers a structure of type **3**, a result that can be attributed to its relatively large volume.

EXPERIMENTAL

NMR studies were performed with a Jeol GSX 270 spectrometer, TMS being used as reference and chemical shifts being stated in parts per million.

Preparation of [Hg_3 (H_2pdm)$_2$(Hpdm) (μ-Cl)$_2$$Cl_3$]

The complex was prepared by refluxing 480 mg (1.80 mmol) mercury(II)chloride and 250 mg (1.80 mmol) 2,6-pyridinedimethanol (H_2pdm) for 3 hours in ethyl acetate (50 mL) in a metal-to-ligand ratio of 1:1. When the mixture was allowed to stand for a few days, a small amount of white crystals separated, which were suitable for X-ray crystallography. Mp 134–136°C; ^{1}H-NMR data (270 MHz, DMSO-d$_6$, ppm): 4.63 (4H, br, s, O-CH$_2$), 5.97 (2H, br, s, OH), 7.40 (2H, d, 3,5-H of py), 7.88 (1H, t, 4-H of py); ^{13}C-NMR data (67.8 MHz, DMSO-d$_6$, ppm): 63.0 (O–CH$_2$), 159.8 (2,6-C of py), 138.1 (4-C of py), 119.4 (3,5-C of py); MS data (20 eV): 272 ($HgCl_2^+$, 57%), 202 (Hg^+, 33%), 138 ($Hpdm^+$, 100%), 121 ($C_7H_7NO^+$, 53%), 92 ($C_6H_6N^+$, 60%), 65 ($C_5H_5^+$, 41%); neither the molecular peak of [Hg(H_2pdm)Cl_2] nor the one of [Hg_3(H_2pdm)$_2$(Hpdm) (μ-Cl)$_2$$Cl_3$] could be observed. The main product of the reaction crystallizes on further evaporation of the solvent. The formula of this compound is (H_2pdm)$HgCl_2$·1/2 $HgCl_2$. Mp 160°C (dec.). Yield: 49%. Found: C, 15.61; H, 1.68; N, 2.52. Calcd: C, 15.42, H, 1.66; N, 2.57. The crystals obtained were not suitable for X-ray crys-

TABLE 1 Fractional Atomic Coordinates and Isotropic Thermal Parameters for [Hg_3(H_2pdm)$_2$(Hpdm)(μ-Cl)$_2$$Cl_3$]

Atom	*x/a*	*y/b*	*z/c*	*U*(*iso*)
Hg(1)	0.28922(8)	0.02721(7)	0.44625(5)	0.0483
Hg(2)	0.48206(7)	0.33598(6)	0.22732(5)	0.0439
Hg(3)	0.95353(7)	0.35393(7)	0.17667(5)	0.0502
Cl(1)	0.3383(5)	−0.1457(5)	0.3416(4)	0.0603
Cl(2)	0.2523(4)	0.2045(4)	0.3160(4)	0.0528
Cl(3)	0.4324(5)	0.5185(4)	0.3167(4)	0.0601
Cl(4)	0.7630(5)	0.4569(5)	0.1203(4)	0.0568
Cl(5)	1.0317(6)	0.1795(5)	0.0803(4)	0.0679
N(1)	0.231(1)	0.115(1)	0.6010(9)	0.0321
N(2)	0.549(1)	0.204(1)	0.1031(9)	0.0329
N(3)	0.962(1)	0.486(1)	0.301(1)	0.0365
O(1)	0.478(1)	0.137(1)	0.4761(9)	0.0467
O(2)	0.090(1)	−0.089(1)	0.5673(9)	0.0461
O(3)	0.617(1)	0.1944(9)	0.2889(8)	0.0357
O(4)	0.413(1)	0.409(1)	0.057(1)	0.0622
O(5)	0.806(1)	0.281(1)	0.3477(8)	0.0379
O(6)	1.137(2)	0.511(2)	0.114(1)	0.0945
C(1)	0.427(2)	0.240(1)	0.536(1)	0.0390
C(2)	0.310(2)	0.203(1)	0.621(1)	0.0344
C(3)	0.280(2)	0.262(1)	0.716(1)	0.0401
C(4)	0.173(2)	0.228(2)	0.793(1)	0.0499
C(5)	0.092(2)	0.138(2)	0.772(1)	0.0408
C(6)	0.125(2)	0.084(1)	0.674(1)	0.0321
C(7)	0.032(2)	−0.007(2)	0.651(1)	0.0452
C(8)	0.659(2)	0.101(1)	0.223(1)	0.0400
C(9)	0.635(2)	0.117(2)	0.114(1)	0.0423
C(10)	0.702(2)	0.045(2)	0.033(1)	0.0535
C(11)	0.674(2)	0.059(2)	−0.063(1)	0.0550
C(12)	0.581(2)	0.144(2)	−0.074(1)	0.0543
C(13)	0.523(2)	0.216(2)	0.008(1)	0.0429
C(14)	0.417(2)	0.302(2)	−0.002(2)	0.0633
C(15)	0.767(1)	0.384(2)	0.407(1)	0.0374
C(16)	0.870(1)	0.484(1)	0.392(1)	0.0255
C(17)	0.865(2)	0.566(1)	0.469(1)	0.0365
C(18)	0.960(2)	0.659(1)	0.452(1)	0.0439
C(19)	1.055(2)	0.661(2)	0.362(1)	0.0401
C(20)	1.053(1)	0.576(1)	0.287(1)	0.0357
C(21)	1.155(2)	0.585(2)	0.181(2)	0.0637

TABLE 2 Selected Bond Lengths and Angles for [Hg_3(H_2pdm)$_2$(Hpdm)(μ-Cl)$_2$$Cl_3$]

Fragment Hg(2)			
Bond Lengths (Å)			
Hg(2)-O(3)	2.364(9)	Hg(2)-Cl(3)	2.314(4)
Hg(2)-N(2)	2.18(1)	Hg(2)-Cl(2)	2.799(5)
Hg(2)-O(4)	2.64(1)	Hg(2)-Cl(4)	3.225(5)
Bond Angles (°)			
O(3)-Hg(2)-N(2)	73.5(4)	Cl(2)-Hg(2)-O(4)	95.0(3)
N(2)-Hg(2)-O(4)	69.9(4)	Cl(2)-Hg(2)-Cl(3)	99.3(2)
O(3)-Hg(2)-O(4)	142.6(4)	Cl(2)-Hg(2)-Cl(4)	173.4(4)
O(3)-Hg(2)-Cl(3)	117.1(3)	Cl(4)-Hg(2)-O(3)	80.0(4)
O(4)-Hg(2)-Cl(3)	96.7(3)	Cl(4)-Hg(2)-N(2)	81.6(4)
N(2)-Hg(2)-Cl(3)	162.5(3)	Cl(4)-Hg(2)-O(4)	87.1(4)
Cl(2)-Hg(2)-O(3)	94.7(3)	Cl(4)-Hg(2)-Cl(3)	86.6(4)
Cl(2)-Hg(2)-N(2)	93.3(4)	Hg(1)-Cl(2)-Hg(2)	111.5(2)
		Hg(2)-Cl(4)-Hg(3)	114.7(4)
Fragment Hg(1)		*Fragment Hg(3)*	
Bond Lengths (Å)			
Hg(1)-Cl(2)	2.633(4)	Hg(3)-Cl(4)	2.571(5)
Hg(1)-Cl(1)	2.330(5)	Hg(3)-Cl(5)	2.330(5)
Hg(1)-O(1)	2.46(1)	Hg(3)-O(6)	2.54(2)
Hg(1)-N(1)	2.21(1)	Hg(3)-N(3)	2.23(1)
Hg(1)-O(2)	2.61(1)	Hg(3)-O(5)	2.50(1)
Bond Angles (°)			
Cl(2)-Hg(1)-Cl(1)	104.1(2)	Cl(4)-Hg(3)-Cl(5)	112.8(2)
Cl(2)-Hg(1)-O(1)	91.1(3)	Cl(4)-Hg(3)-O(6)	102.9(6)
Cl(2)-Hg(1)-N(1)	102.9(3)	Cl(4)-Hg(3)-N(3)	96.7(3)
Cl(2)-Hg(1)-O(2)	119.8(3)	Cl(4)-Hg(3)-O(5)	91.5(3)
Cl(1)-Hg(1)-O(1)	115.4(3)	Cl(5)-Hg(3)-O(6)	103.5(5)
Cl(1)-Hg(1)-N(1)	152.0(3)	Cl(5)-Hg(3)-N(3)	150.5(3)
Cl(1)-Hg(1)-O(2)	90.0(3)	Cl(5)-Hg(3)-O(5)	107.4(3)
O(1)-Hg(1)-N(1)	71.1(4)	O(6)-Hg(3)-N(3)	68.0(5)
O(1)-Hg(1)-O(2)	134.7(3)	O(6)-Hg(3)-O(5)	137.4(4)
N(1)-Hg(1)-O(2)	70.2(4)	N(3)-Hg(3)-O(5)	70.6(4)

TABLE 3 Deviations from the Chelate Mean Planes

Atom	*Δ(Å)*	*Atom*	*Δ(Å)*	*Atom*	*Δ(Å)*
Plane 1[a]		*Plane 2*[b]		*Plane 3*[c]	
N(1)	0.002	N(2)	0.013	N(3)	0.002
C(2)	0.011	C(9)	−0.022	C(16)	0.000
C(3)	−0.017	C(10)	0.008	C(17)	0.005
C(4)	0.011	C(11)	0.013	C(18)	−0.011
C(5)	0.002	C(12)	−0.022	C(19)	0.013
C(6)	−0.009	C(13)	0.009	C(20)	−0.008
Deviations from the mean plane (Å)					
C(1)	−0.025	C(8)	−0.078	C(15)	−0.002
O(1)	0.691	O(3)	0.242	O(5)	0.509
O(2)	0.356	O(4)	0.595	O(6)	−0.237
C(7)	−0.103	C(14)	−0.105	C(21)	−0.085
Hg(1)	−0.050	Hg(2)	0.379	Hg(3)	−0.127

[a] Plane 1, $6.70766X - 7.42661Y + 6.44275Z = 4.563$; X, Y, Z are orthogonal coordinates w.r.t. axes a, b, c^*; Δ is the deviation from the plane.

[b] Plane 2, $7.20709X + 7.39634Y - 1.02532Z = 5.347$.

[c] Plane 3, $7.37758X - 6.39634Y + 7.32912Z = 6.193$.

tallography, because they are highly twinned. ^{1}H and ^{13}C NMR data are identical to those of the minor product.

X-ray Crystallography

Data for the X-ray crystallography of $[Hg_3(H_2pdm)_2(Hpdm)\ (\mu\text{-}Cl)_2Cl_3]$ were collected on an ENRAF-NONIUS CAD4 diffractometer, $\lambda(MoK_\alpha) = 0.710690$ Å; monochromator: graphite, $T = 293$ K, ω-2θ scan, range $2° < \theta < 27°$.

Crystal Data. Colorless, rectangular crystals of $[Hg_3(H_2pdm)_2(Hpdm)\ (\mu\text{-}Cl)_2Cl_3]$ ($M = 1195.49$ gmol^{-1}) crystallize in the triclinic space group P-1 (no. 2), crystal dimensions $0.20 \times 0.20 \times 0.36$ mm^3, $a = 10.640(1)$, $b = 10.818(2)$, $c = 13.159(2)$ Å, $\alpha = 88.480(5)$, $\beta = 75.067(4)$, $\gamma = 89.736(5)°$, $V = 1463.0(4)$ Å^3 by least-squares refinement on diffractometer angles for 24 automatically centered reflections ($10° < \theta < 11°$), $Z = 2$, $\rho_{calcd} = 2.71$ Mgm^{-3}, $\mu = 16.2$ mm^{-1}. The crystal was mounted in a Lindeman tube. Monitoring of two check reflections showed a significant intensity decay of about 39% during data-collection. The data were rescaled with respect to the standards. A total of 6709 reflections was measured, of which 6365 were independent, and of these, 3678 were considered observed [$F > 3\sigma(F)$], an absorption correction being applied (DIFABS, min: 0.63, max: 1.27), and corrections being made for Lorentz and polarization effects.

Solution and Refinement. Direct methods (SHELXS-86) were used for structure solution. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were calculated, assuming that the OH hydrogens are coplanar with the remainder of the 2,6-pyridinedimethanol ligand, and refined with an overall isotropic thermal parameter (CRYSTALS, version 9, 1994). $R = 0.044$, $R_w = 0.044$ from 3678 reflections with $F > 3\sigma(F)$ for 345 variables against $|F|$, $w = 1/\sigma^2(F)$, $s = 4.64$. The largest residual electron density peak/hole in the final difference map was $\rho_{max} = 1.97$, $\rho_{min} = -1.49$ e/Å^3, max Δ/σ shift 0.006.

Final fractional atomic coordinates are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2. Deviations from the chelate mean planes are listed in Table 3.

DISCUSSION

The crystal structure of $[Hg_3(H_2pdm)_2(Hpdm)\ (\mu\text{-}Cl)_2Cl_3]$ consists of discrete trimeric molecules. As can be seen from Figure 1, the central [Hg(2)(Hpdm)Cl] fragment in the molecular structure is flanked by two $[Hg(H_2pdm)Cl_2]$ units via bridging chlorine atoms [Hg(2)–Cl(2) 2.799(5) Å, Hg(2)–Cl(4) 3.225(5) Å, Cl(2)–Hg(2)–Cl(4) 173.4(4)°]. Thereby, the $[Hg(H_2pdm)Cl_2]$ moieties are located in a *cis*-configuration with respect to the Cl(2)–Hg(2)–Cl(4) axis.

The central mercury atom Hg(2) is covalently bonded to chlorine Cl(3) and oxygen O(3). The Hg(2)–Cl(3) bond length is 2.314(4) Å, a value that corresponds to the Hg–Cl bond length in solid $HgCl_2$ [2.626(21) Å] [2]. The covalency of the Hg(2)–O(3) bond with a length of 2.364(9) Å is confirmed by comparison with the other five Hg–OH bond lengths in the structure (Table 2), being coordinative [2.46(1)–2.64(1) Å]. The Hg(2)–O(4) bond is thereby the longest one. Furthermore, electron density typical for hydrogen atoms could only be located by difference Fourier maps in the case of O(1), O(2), O(4), O(5), and O(6).

The formation of the covalent Hg(2)–O(3) bond can be attributed to the reaction of $HgCl_2$ and H_2pdm under removal of one HCl molecule. In the ^{1}H- and ^{13}C-NMR spectra, only one set of signals is observed for the two differently bonded tridentate ligands [Hg(1), Hg(3) ↔ Hg(2)], indicating that the trimer is dissociated in solution (DMSO-d_6). Coordination to $HgCl_2$ can be seen from the ^{1}H-NMR spectrum, where the hydrogen atoms of the OH groups are shifted to low field by 0.6 ppm with respect to H_2pdm. The coupling between the OCH_2 group and the OH hydrogen atoms disappeared, and both signals broadened significantly due to a rapid interchange and the quadrupolar moment of mercury [9].

Due to the tridentate chelation of the ligand, the coordinative Hg–N bonds are extremely short

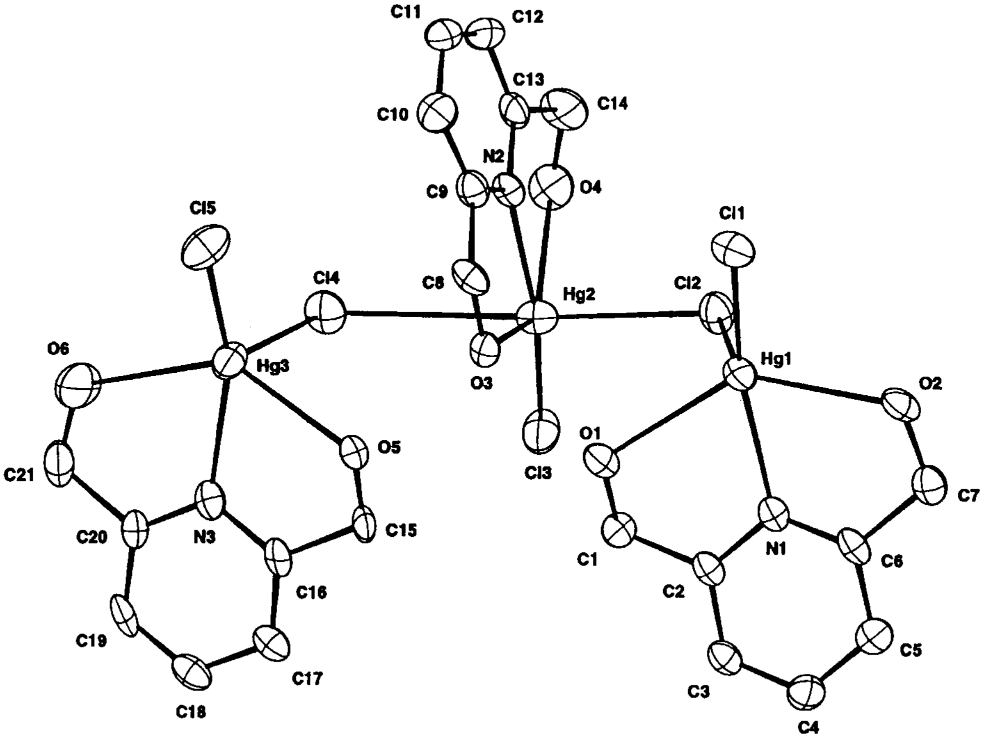


FIGURE 1 Molecular structure of [Hg_3 ($H_2pdm)_2$ (Hpdm) (μ-$Cl)_2Cl_3$].

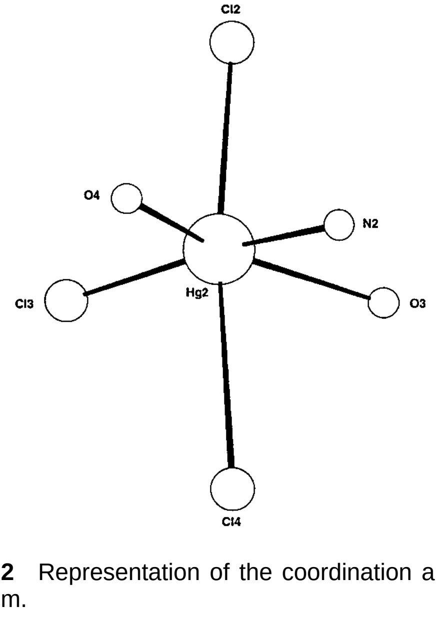


FIGURE 2 Representation of the coordination around the Hg(2) atom.

[Hg(1)–N(1) 2.21(1) Å, Hg(2)–N(2) 2.18(1) Å, Hg(3)–N(3) 2.23(1) Å], when compared to $(py)_2$-$HgCl_2$ (2.60 Å in the [2+2+2 (N)] coordination mode and 2.266(6) Å in the [0+4+2 (N)] coordination mode) [10–12]. In {(Nicotine)·$HgCl_2\}_n$, the Hg–N(py) bond length is 2.454(13) Å [13].

The mercury chlorine bond lengths of the terminal chlorines Cl(1) and Cl(5) [Hg(1)–Cl(1) 2.330(5) Å, Hg(3)–Cl(5) 2.330(5) Å] are not significantly different from the Hg(2)–Cl(3) bond length [2.314(4) Å] of the central unit. On the other hand, the bridging chlorines present somewhat elongated bond lengths, [Hg(1)–Cl(2) 2.633(4) Å, Hg(3)–Cl(4) 2.571(5) Å].

A closer examination of the environment around the mercury atoms shows that there exist two different coordination spheres. While the central Hg(2) atom is located in a distorted octahedral polyhedron, Hg(1) and Hg(3) are placed in distorted square-pyramidal environments. As can be seen from Figure 2, the equatorial positions of the octahedron are occupied by the ligand and the terminal chlorine atom. The axial substituents consist of the bridging chlorines Cl(2) and Cl(4), the second Hg–Cl bond being significantly elongated [Hg(2)–Cl(2) 2.799(5) Å, Hg(2)–Cl(4) 3.225(5) Å]. As an upper limit for Hg···Cl bonding, a value of 3.35 Å is adopted [8]. Consequently, as can be seen from a comparison of the bond angles between the axial chlorine atoms and the equatorial substituents (Table 2), the upper part of the octahedron is distorted in the direction of a square-pyramidal arrangement. The average value of the Cl–Hg–X_{eq} bond angle is 95.6(3)° for the upper part and 83.8(4)° for the lower part.

Five-coordination occupies a special position in

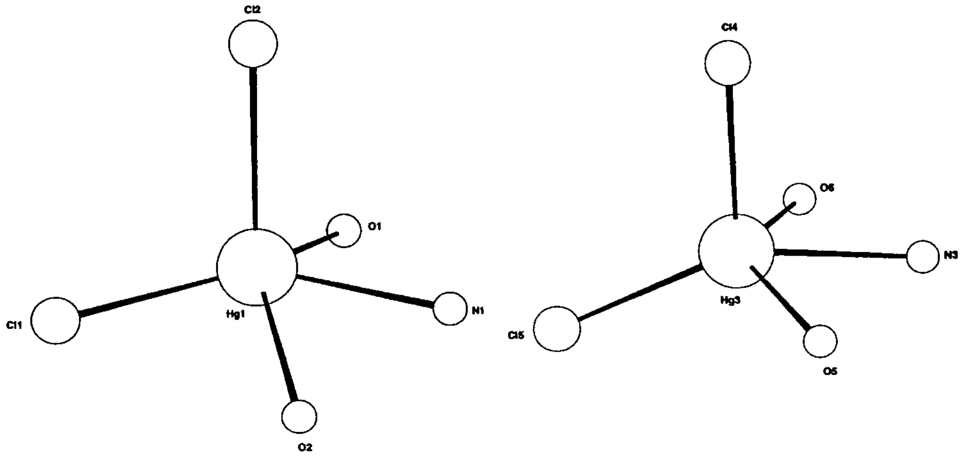


FIGURE 3 Representation of the square-pyramidal coordination around the Hg(1) and Hg(3) atoms.

the coordination geometry of Hg(II), because two different polyhedrons, possessing a trigonal-bipyramidal or a square-pyramidal structure geometry, can be formed. Normally, for d^{10} metal ions, the trigonal-bipyramidal polyhedron with D_{3h}-symmetry is preferred [14–25]. Thus, only a few square-pyramidal structures with C_{4v}-symmetry are known [26–28]. In general, all these structures are distorted due to the presence of different atom types and crystal-packing effects. Despite this, real intermediates between the two structure types are rare [29]. In the present example, the rigid, tridentate ligand, having an overall bite significantly greater than 120°, leads to the formation of a highly distorted square-pyramidal polyhedron. The apical positions of the distorted square-pyramidal polyhedrons are occupied by the bridging chlorines Cl(2) and Cl(4), respectively (Figure 3). Their bond lengths are significantly different [Hg(1)–Cl(2) 2.633(4) Å, Hg(3)–Cl(4) 2.571(5) Å]. The different puckering of the chelate rings (Table 3), probably due to crystal-packing effects, leads to different bond angles in the two square-pyramidal environments. The average values of the Cl_{apical}–Hg–X_{basal} bond angles are 104.5(3)° for fragment Hg(1) and 101.0(3)° for fragment Hg(3), being significantly lower than the idealized value of 109°. The coordination geometry of mercury(II)chloride systems can be described by a sequence of numbers that indicates the bonding of the different atoms present in the molecule under study. The first two numbers correspond thereby to the covalent and coordinative Hg–Cl bonds [8]. According to conventional nomenclature, the coordination of the Hg(2) mercury atom in the present molecule can be described as a [1 + 2 + 2(0) + 1(N)] coordination mode, while Hg(1) and Hg(3) correspond to a [2 + 0 + 2(0) + 1(N)] type. Neither of the coordination modes have been reported so far [8].

CONCLUSIONS

The present study has shown that $HgCl_2$ prefers to form a bicyclic monochelate complex upon reaction with 2,6-pyridinedimethanol, as against the results with phenylboronic acid and dichlorodimethylsilane. In comparison to the diorganotin(IV) derivative **3**, the Hg–O bonds between the metal atoms and the ligand are only coordinative, with the exception of the central Hg(Hpdm)Cl fragment, where one of the two Hg–O bonds is covalent.

ACKNOWLEDGMENTS

The authors thank Prof. Dr. R. Santillan and Prof. Dr. M. Rosales for critical reading of the manuscript. H. H. thanks the Secretary of Foreign Relations (S.R.E.), and N. F. thanks CONACYT for financial support.

REFERENCES

[1] N. Farfán, D. Castillo, P. Joseph-Nathan, R. Contreras, L. V. Szentpály, *J. Chem. Soc. Perkin Trans., 2,* 1992, 527.

[2] N. Farfán, R. Contreras, *J. Chem. Soc., Perkin Trans., 2,* 1988, 1787.

[3] L. A. Torres, A. Pérez, N. Farfán, D. Castillo, R. L. Santillan, *J. Chem. Thermodyn., 26,* 1994, 337.

[4] H. Höpfl, N. Farfán, *J. Organomet. Chem., 547,* 1997, 71.

[5] T. K. Prakasha, A. Chandrasekaran, R. O. Day, R. R. Holmes, *Inorg. Chem., 35,* 1996, 4342.

[6] M. Gielen, M. Bouâlam, M. Biesemans, B. Mahieu, R. Willem, *Heterocycles, 34,* 1992, 549.

[7] K. Brodersen, H.-U. Hummel: in G. Wilkinson (ed): *Comprehensive Coordination Chemistry,* Pergamon, Oxford, Vol. 5, p. 1047 (1987) and references therein.

[8] D. A. House, W. T. Robinson, *Coord. Chem. Rev., 135/136,* 1994, 533 and references therein.
[9] B. Wrackmeyer, R. Contreras, *Annual Rept. NMR Spectroscopy, 24,* 1992, 5361.
[10] D. Grdenic, I. Krstanovic, *Ark. Kemi, 27,* 1955, 143; *Chem. Abstr., 50,* 1956, 5361.
[11] J. D. Dunitz, *Acta Crystallogr., 10,* 1957 307.
[12] A. J. Canty, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.,* 1982, 15.
[13] M. R. Udupa, B. Krebs, *Inorg. Chim. Acta, 40,* 1980, 161.
[14] L. P. Battaglia, A. B. Corradi, L. Antolini, T. Manfredini, L. Menabue, G. C. Pellacani, G. Ponticelli, *J. Chem. Soc. Dalton Trans.,* 1986, 2529.
[15] P. D. Brotherton, P. C. Healy, C. L. Raston, A. H. White, *J. Chem. Soc. Dalton Trans.,* 1973, 334.
[16] W. J. Kozarek, Q. Fernando, *Inorgan. Chem., 12,* 1973, 2129.
[17] M. Sandström, D. H. Liem, *Acta Chem. Scand., A32,* 1978, 509.
[18] P. Biscarini, L. Fusina, G. Nivellini, G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* 1977, 664.
[19] K. Weidenhammer, M. L. Ziegler, *Z. Anorg. Allg. Chem., 434,* 1977, 152.
[20] S. Menzer, E. C. Hillgeris, B. Lippert, *Inorg. Chim. Acta, 211,* 1993, 221.
[21] M. J. Adams, D. C. Hodgkin, U. A. Raebur, *J. Chem. Soc. A,* 1970, 2632.
[22] M. Sakakibana, Y. Yonemura, Z. Tanaka, S. Matsumoto, K. Fukuyama, H. Matsuura, H. Murata, *J. Mol. Struct., 69,* 1980, 53.
[23] S. Kulpe, *Z. Anorg. Allg. Chem., 349,* 1967, 314.
[24] N. A. Bell, M. Goldstein, T. Jones, I. W. Nowell, *Acta Crystallogr., B36,* 1980, 708.
[25] C. Stalhandske, F. Zintl, *Acta Crystallogr., C42,* 1986, 1449.
[26] P. Biscarini, L. Fusina, G. Nivellini, G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* 1981, 1024.
[27] F. Genet, J. C. Leguen, *Acta Crystallogr., B25,* 1969, 2029.
[28] P. Biscarini, L. Fusina, G. D. Nivellini, A. Magina, G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* 1973, 159.
[29] X.-M. Chen, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.,* 1992, 1585.