Crystal Structure Determination of the Complexes of Di-methylammonium Chloride and Mercury(II) Chloride: $(CH_3)_2NH_2HgCl_3$, $\{(CH_3)_2NH_2\}_2HgCl_4$ and $(CH_3)_2NH_2Hg_2Cl_5$

A. BEN SALAH*, J. W. BATS, H. FUESS and A. DAOUD*

Institut für Kristallographie der Universität, Senckenberganlage 30, 6000 Frankfurt am Main 1, F.R.G.

Received April 23, 1982

Introduction

A great variety of compounds are formed by the reaction of substituted ammonium halogenides with metal halogenides. General formulae are $R_xNH_{4-x}MX_3$ and $(R_xNH_{4-x})_2MX_4$, with R = an aliphatic or aromatic hydrocarbon, M = metal, X = Cl, Br, I. These substances exhibit interesting structural and physical properties. The structures of most of these compounds show successive phase transitions and quite often incommensurate phases (*e.g.* $\{N(CH_3)_4\}_2ZnCl_4$ [1]). The phase transitions are mainly due to order–disorder in the substituted ammonium group. As an example of the physical properties we may mention tetramethylammonium manganese chloride which was extensively studied as a model substance for low dimensional magnetism [2].

A point of further interest besides the study of phase transition in the mercury compounds, is the coordination of Hg(II). Due to closed d-shell and a relatively large volume, Hg(II) may accommodate different numbers of ligands; a distinction between bonded and non-bonded atoms surrounding mercury is, however, not always an evident choice. For instance, a marked preference is observed for linear two coordination, forming a $HgCl_2$ unit which is similar to the structure of $HgCl_2$ [3]. In addition there are two or four equatorial weak interactions with much longer Hg–Cl distances. The distances are in the range of 2.25–2.37 for the 'pseudo molecule' with a Cl–Hg–Cl angle only slightly smaller than 180°, while the weaker interactions range from 2.70–3.10 Å. In the case of four ligands a distorted octahedral coordination around mercury is formed. Regular octahedral coordination is rare and has been observed for complexes where the ligands are relatively hard oxygen atoms [4] and for ternary fluorides [5]. Other common coordination numbers are 3 (trigonal), 4 (tetrahedral) and 5 (trigonal bipyramidal) [4, 6]. In the special case of methylammonium mercury chlorides three types of compounds are realized, namely $Met_xNH_{4-x}HgCl_3$, $\{Met_xNH_{4-x}\}_2HgCl_4$ and $Met_xNH_{4-x}Hg_2Cl_5$. We have already reported on the structures of the mono-

*Permanent address: Département de chimie, Faculté des Sciences et Techniques, Sfax, Tunisia.

TABLE I. Crystal Data.

	$(CH_3)_2NH_2HgCl_3$	$\{(CH_3)_2NH_2\}_2HgCl_4$	$(CH_3)_2NH_2Hg_2Cl_5$
Lattice	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a Å	8.851(1)	7.946(1)	10.434(1)
b Å	20.139(2)	11.332(2)	6.948(1)
c Å	13.757(2)	14.874(2)	16.279(2)
β °	92.15(1)	95.66(1)	103.74(1)
V Å^3	2450(1)	1332.7(5)	1146.4(3)
Z	12	4	4
D_{calc} g cm^{-3}	2.871	2.166	3.618
D_{obs}	2.78(2)	2.20(2)	3.68(2)

0020-1693/82/0000-0000/$02.75

TABLE II. Experimental Conditions.

	$(CH_3)_2NH_2HgCl_3$	$\{(CH_3)_2NH_2\}_2HgCl_4$	$(CH_3)_2NH_2Hg_2Cl_5$
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.50	0.54	0.54
linear absorption coefficient [cm^{-1}]	201	125	284
transmission range for absorption	0.085–0.158	0.216–0.363	0.045–0.202
total number of reflections	4444	4198	3879
independent reflections	2355	1687	1572
number of variables	200	101	92
R(F)	0.064	0.032	0.035
$R_w(F)$	0.064	0.033	0.033
$\{\Sigma w(F_o - F_c)^2/(n_o - n_v)\}^{1/2}$	2.33	0.87	0.96

methylammonium compounds [7]. We describe here structure and mercury coordination of the dimethyl group of compounds.

Experiments and Structure Determination

Single crystals of $(CH_3)_2NH_2HgCl_3$ and $\{(CH_3)_2NH_2\}_2HgCl_4$ were obtained by slow evaporation of a mixture of alcohol and acetone containing stoichiometric amounts of $(CH_3)_2NH_2Cl$ and $HgCl_2$. Single crystals of $(CH_3)_2NH_2Hg_2Cl_5$ were obtained in a similar way from a mixture of acetone and water. The crystal growth of $(CH_3)_2NH_2HgCl_3$ turned out to be rather difficult. Of several attempts, only one led to crystals of the desired compound [8].

Precession photographs showed all three substances to be monoclinic with space group $P2_1/n$. A summary of the crystal data is given in Table I. Data were collected on an Enraf-Nonius CAD4 diffractometer with monochromatic MoK_α radiation (Table II). All calculations were performed with the SDP program package on a PDP11/34 computer. Lists of observed and calculated structure factors can be obtained from the authors.

$(CH_3)_2NH_2HgCl_3$

A crystal with dimensions 0.11 × 0.128 × 0.56 mm was used for the measurements. Reflections were measured in a hemisphere of reciprocal space up to $2\theta = 40°$ with an $\omega/2\theta$ scan. Three standard reflections remeasured repeatedly during the data collection showed intensity decreases of about 5%. This effect was accompanied by a broadening of several reflection profiles during the X-ray irradiation. Not all three standard reflections changed in the same way, so that no correction was made for the decay of the crystal. Each reflection was corrected for absorption by a numerical integration procedure in which the crystal was divided in 8 × 8 × 8 gaussian grid points. The equivalent reflections were averaged. The structure was determined by Patterson and Fourier techniques and refined by least-squares methods. A Fourier synthesis revealed that one of the three independent dimethylammonium groups was disordered, resulting in two positions for the N atom. No hydrogen atoms could be located. For those of the ammonium group, positions were calculated suggesting N–H distances of 0.96 Å and tetrahedral angles about the N atoms. They were included in the least-squares refinement but were not varied. A final difference synthesis showed peaks of 2.5 e/Å^3 near the Hg atoms, but was otherwise featureless. The positional and anisotropic thermal parameters of the atoms are reported in Table III.

$\{(CH_3)_2NH_2\}_2HgCl_4$

A crystal with dimensions 0.090 × 0.13 × 0.18 mm was selected for the measurements. Reflections were measured in a hemisphere of reciprocal space up to $2\theta = 45°$. Three standard reflections repeatedly remeasured during the data collection did not show any significant fluctuations. The data were processed as for the previous compound. The structure was determined by Patterson and Fourier techniques. The positions of the hydrogen atoms attached to the nitrogen atoms were again calculated. The final difference Fourier synthesis was featureless.

$(CH_3)_2NH_2Hg_2Cl_5$

The data collection crystal had dimensions 0.066 × 0.106 × 0.35 mm. Reflections were measured in a hemisphere of reciprocal space up to $2\theta = 45°$. The intensities of three standard reflections decreased about 10% during the measurement. The data were rescaled with respect to the standards. The data processing and structure determination were as for the previous compounds.

TABLE III. Positional and Thermal Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
$(CH_3)_2NH_2HgCl_3$									
Hg(1)	0.2379(1)	0.16094(4)	0.42555(6)	0.0822(7)	0.0467(5)	0.0617(5)	−0.0038(5)	−0.0133(5)	−0.0073(4)
Hg(2)	0.2201(1)	−0.00182(4)	0.75287(5)	0.0675(5)	0.0522(5)	0.0513(4)	0.0068(4)	0.0068(4)	−0.0040(4)
Hg(3)	0.3184(1)	0.84731(4)	0.09277(6)	0.0805(6)	0.0482(4)	0.0562(4)	0.0028(4)	−0.0053(5)	0.0011(4)
Cl(1)	0.9586(6)	0.7497(2)	0.4995(4)	0.084(4)	0.045(3)	0.087(3)	0.006(3)	0.036(3)	0.010(2)
Cl(2)	0.3847(6)	0.9171(2)	0.6981(4)	0.081(4)	0.051(3)	0.075(3)	0.006(3)	0.021(3)	−0.012(3)
Cl(3)	0.2671(7)	0.7895(3)	0.2362(4)	0.091(4)	0.078(4)	0.071(3)	0.003(3)	0.023(3)	0.018(3)
Cl(4)	0.0798(6)	0.5905(2)	0.6539(4)	0.054(3)	0.055(3)	0.071(3)	0.013(3)	−0.004(4)	0.011(2)
Cl(5)	0.5116(6)	0.4573(3)	0.3301(4)	0.060(3)	0.065(3)	0.078(3)	0.002(3)	0.009(3)	0.015(3)
Cl(6)	0.4087(7)	0.5969(3)	0.1823(4)	0.079(4)	0.068(3)	0.064(3)	0.010(3)	−0.005(3)	0.013(3)
Cl(7)	0.2685(7)	0.4166(3)	0.5331(4)	0.091(4)	0.076(3)	0.064(3)	−0.007(3)	0.010(3)	−0.019(3)
Cl(8)	0.2880(9)	0.5712(3)	0.9162(4)	0.162(7)	0.070(4)	0.057(3)	−0.005(4)	−0.005(4)	−0.020(3)
Cl(9)	0.0423(7)	0.7106(3)	0.0105(5)	0.079(4)	0.090(4)	0.106(4)	0.021(4)	0.000(4)	0.009(4)
N(1)	0.278(2)	0.5781(9)	0.453(1)	0.09(1)	0.09(1)	0.07(1)	0.01(1)	0.00(1)	0.01(1)
N(2)	0.267(3)	0.2186(10)	0.718(1)	0.18(2)	0.10(1)	0.06(1)	0.06(1)	0.00(1)	−0.01(1)
N(3)*	0.205(3)	0.9454(13)	0.415(2)	0.03(2)	0.04(2)	0.13(2)	0.01(1)	−0.07(2)	0.02(2)
N(3')*	0.297(5)	0.9326(23)	0.461(3)	0.15(4)	0.14(3)	0.07(2)	0.03(3)	−0.03(3)	−0.05(2)
C(1)	0.334(3)	0.649(1)	0.455(2)	0.15(2)	0.04(1)	0.09(2)	−0.04(1)	0.04(2)	−0.02(1)
C(2)	0.146(3)	0.565(1)	0.389(2)	0.06(1)	0.13(2)	0.07(1)	−0.02(1)	−0.02(1)	−0.01(1)
C(3)	0.354(3)	0.277(1)	0.725(2)	0.15(2)	0.05(1)	0.11(2)	−0.03(1)	−0.02(2)	0.00(1)
C(4)	0.127(3)	0.220(1)	0.769(2)	0.12(2)	0.11(2)	0.15(2)	0.05(1)	0.09(1)	0.07(1)
C(5)	0.361(2)	0.955(1)	0.373(2)	0.11(2)	0.09(2)	0.14(2)	−0.02(1)	0.09(1)	0.02(1)
C(6)	0.172(3)	0.891(1)	0.461(2)	0.09(2)	0.12(2)	0.12(2)	−0.05(1)	0.03(1)	0.00(2)
H(11)	0.2548	0.5647	0.5192	0.095					
H(12)	0.3605	0.5487	0.4333	0.095					
H(21)	0.3269	0.1800	0.7411	0.095					
H(22)	0.2416	0.2081	0.6480	0.095					
H(31)*	0.1299	0.9499	0.3620	0.095					
H(32)*	0.1875	0.9829	0.4597	0.095					
H(31')*	0.2723	0.9717	0.4959	0.095					
H(32')*	0.3767	0.9088	0.4958	0.095					
				*population 0.5					
$\{(CH_3)_2NH_2\}_2HgCl_4$									
Hg	0.28532(3)	0.20175(3)	0.05075(2)	0.0489(1)	0.0468(2)	0.0548(1)	0.0033(1)	0.0050(1)	−0.0001(2)
Cl(1)	0.2897(2)	−0.0150(2)	0.0539(1)	0.079(1)	0.043(1)	0.071(1)	−0.002(1)	0.009(1)	0.008(1)
Cl(2)	0.3272(2)	0.2693(2)	0.8923(1)	0.068(1)	0.055(1)	0.0509(9)	−0.003(1)	0.0025(9)	0.0079(9)

(continued overleaf)

TABLE III. *(continued)*

Atom	x	y	z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Cl(3)	0.9545(2)	0.7769(2)	0.3622(1)	0.062(1)	0.056(1)	0.073(1)	0.002(1)	−0.017(1)	0.007(1)
Cl(4)	0.5274(2)	0.2101(2)	0.5941(1)	0.0558(9)	0.075(1)	0.087(1)	−0.015(1)	0.0179(9)	0.007(1)
N(1)	0.2983(8)	−0.0140(6)	0.8295(4)	0.080(4)	0.058(4)	0.052(3)	0.005(4)	−0.006(3)	0.005(4)
N(2)	0.2297(8)	0.1839(6)	0.4315(5)	0.061(3)	0.047(4)	0.087(4)	0.005(3)	0.007(3)	−0.016(4)
C(1)	0.1185(10)	0.5164(9)	0.7503(5)	0.080(5)	0.083(6)	0.048(4)	0.006(5)	0.023(4)	0.007(5)
C(2)	0.3868(9)	0.4874(9)	0.6824(6)	0.051(4)	0.079(6)	0.101(6)	0.011(4)	0.004(4)	−0.012(6)
C(3)	0.2870(12)	0.5548(10)	0.0502(7)	0.110(7)	0.058(6)	0.119(8)	−0.004(6)	−0.005(7)	0.006(6)
C(4)	0.1979(13)	0.7136(10)	0.1533(7)	0.104(6)	0.097(8)	0.095(6)	0.002(6)	0.043(5)	0.015(6)
H(11)	0.1637	0.5403	0.6230	0.070					
H(12)	0.1632	0.4097	0.6502	0.070					
H(21)	0.2005	0.7175	0.0199	0.070					
H(22)	0.3791	0.7190	0.0697	0.070					
$(CH_3)_2NH_2Hg_2Cl_5$									
Hg(1)	0.93451(3)	0.37910(6)	0.59382(2)	0.0408(2)	0.0434(2)	0.0486(2)	−0.0005(2)	0.0188(1)	−0.0001(2)
Hg(2)	0.85220(3)	0.11443(6)	0.35170(2)	0.0395(2)	0.0428(2)	0.0464(2)	−0.0031(2)	0.0161(1)	−0.0021(2)
Cl(1)	0.3570(2)	0.0359(3)	0.7720(1)	0.036(1)	0.037(1)	0.042(1)	−0.000(1)	0.0008(1)	−0.0071(9)
Cl(2)	0.2678(2)	−0.0127(4)	0.1488(1)	0.041(1)	0.054(1)	0.059(1)	0.004(1)	0.0202(9)	0.009(1)
Cl(3)	0.0823(2)	0.2582(3)	0.5194(1)	0.041(1)	0.041(1)	0.050(1)	0.005(1)	0.0161(9)	0.005(1)
Cl(4)	0.7201(2)	0.2168(4)	0.4419(1)	0.042(1)	0.055(1)	0.047(1)	−0.004(1)	0.0155(9)	−0.008(1)
Cl(5)	0.4746(2)	0.4762(4)	0.1984(1)	0.046(1)	0.045(1)	0.059(1)	−0.012(1)	0.0227(9)	−0.014(1)
N	0.5464(8)	0.182(1)	0.6552(5)	0.055(5)	0.049(5)	0.055(4)	−0.015(4)	0.013(4)	−0.004(4)
C(1)	0.605(1)	0.012(2)	0.6248(6)	0.051(6)	0.058(7)	0.069(6)	0.005(6)	0.013(5)	−0.004(5)
C(2)	0.948(1)	0.218(2)	0.0877(7)	0.066(7)	0.055(7)	0.073(6)	−0.006(6)	−0.014(6)	−0.016(5)
H(1)	0.6156	0.2715	0.6801	0.057					
H(2)	0.5047	0.1431	0.6994	0.057					

TABLE IV. Bond Distances (in Å) and Angles (in °) (e.s.d.'s in parentheses).

$(CH_3)_2NH_2HgCl_3$

Hg(1)–Cl(6)	2.325(4)	Cl(6)–Hg(1)–Cl(9)	156.5(2)
Hg(1)–Cl(9)	2.330(4)	Cl(6)–Hg(1)–Cl(1)	105.0(1)
Hg(1)–Cl(1)	2.732(3)	Cl(6)–Hg(1)–Cl(8)	94.4(1)
Hg(1)–Cl(8)	2.846(3)	Cl(9)–Hg(1)–Cl(1)	96.3(1)
Hg(2)–Cl(2)	2.332(3)	Cl(9)–Hg(1)–Cl(8)	94.2(2)
Hg(2)–Cl(5)	2.342(3)	Cl(1)–Hg(1)–Cl(8)	93.4(1)
Hg(2)–Cl(4)	2.840(3)	Cl(2)–Hg(2)–Cl(5)	158.0(1)
Hg(2)–Cl(8)	2.750(3)	Cl(2)–Hg(2)–Cl(4)	102.6(1)
Hg(3)–Cl(3)	2.350(3)	Cl(2)–Hg(2)–Cl(8)	95.6(1)
Hg(3)–Cl(7)	2.332(4)	Cl(5)–Hg(2)–Cl(4)	91.9(1)
Hg(3)–Cl(1)	2.668(3)	Cl(5)–Hg(2)–Cl(8)	100.5(1)
Hg(3)–Cl(4)	2.736(3)	Cl(4)–Hg(2)–Cl(8)	91.6(1)
N(1)–C(1)	1.51(2)	Cl(3)–Hg(3)–Cl(7)	148.4(2)
N(1)–C(2)	1.46(2)	Cl(3)–Hg(3)–Cl(1)	98.6(1)
N(2)–C(3)	1.42(2)	Cl(3)–Hg(3)–Cl(4)	99.0(1)
N(2)–C(4)	1.45(2)	Cl(7)–Hg(3)–Cl(1)	103.1(1)
N(3)–C(5)	1.53(3)	Cl(7)–Hg(3)–Cl(4)	101.9(1)
N(3)–C(6)	1.31(3)	Cl(1)–Hg(3)–Cl(4)	94.6(1)
N(3')–C(5)	1.42(4)	C(1)–N(1)–C(2)	116(1)
N(3')–C(6)	1.39(4)	C(3)–N(2)–C(4)	115(1)
		C(5)–N(3)–C(6)	120(2)
		C(5)–N(3')–C(6)	122(3)

$\{(CH_3)_2NH_2\}_2HgCl_4$

Hg–Cl(1)	2.457(2)	Cl(1)–Hg–Cl(2)	108.49(7)
Hg–Cl(2)	2.530(2)	Cl(1)–Hg–Cl(3)	108.89(8)
Hg–Cl(3)	2.479(2)	Cl(1)–Hg–Cl(4)	114.70(8)
Hg–Cl(4)	2.424(2)	Cl(2)–Hg–Cl(3)	101.73(8)
N(1)–C(1)	1.46(1)	Cl(2)–Hg–Cl(4)	108.38(8)
N(1)–C(2)	1.46(1)	Cl(3)–Hg–Cl(4)	113.75(8)
N(2)–C(3)	1.50(2)	C(1)–N(1)–C(2)	115.5(8)
N(2)–C(4)	1.48(1)	C(3)–N(2)–C(4)	115.3(8)

$(CH_3)_2NH_2Hg_2Cl_5$

Hg(1)–Cl(2)	2.330(3)	Cl(2)–Hg(1)–Cl(3)	171.58(8)
Hg(1)–Cl(3)	2.332(2)	Cl(2)–Hg(1)–Cl(1)	93.21(8)
Hg(1)–Cl(1)	2.904(2)	Cl(2)–Hg(1)–Cl(5)	97.30(9)
Hg(1)–Cl(5)	2.972(2)	Cl(3)–Hg(1)–Cl(1)	93.21(7)
Hg(1)–Cl(3)	3.102(2)	Cl(3)–Hg(1)–Cl(5)	88.74(7)
Hg(1)–Cl(4)	3.124(2)	Cl(1)–Hg(1)–Cl(5)	84.40(7)
Hg(2)–Cl(4)	2.350(2)	Cl(4)–Hg(2)–Cl(5)	162.04(8)
Hg(2)–Cl(5)	2.357(2)	Cl(4)–Hg(2)–Cl(1)	95.16(8)
Hg(2)–Cl(1)	2.797(2)	Cl(4)–Hg(2)–Cl(1)	96.08(8)
Hg(2)–Cl(1)	2.760(2)	Cl(5)–Hg(2)–Cl(1)	97.48(8)
N–C(1)	1.47(1)	Cl(5)–Hg(2)–Cl(1)	95.45(8)
N–C(2)	1.49(1)	Cl(1)–Hg(2)–Cl(1)	95.08(4)
		C(1)–N–C(2)	113.4(8)

Discussion

Bond distances and angles for the three compounds are given in Table IV. Diagrams showing the arrangement of the atoms in the unit cells are given in Figs. 1, 2 and 3.

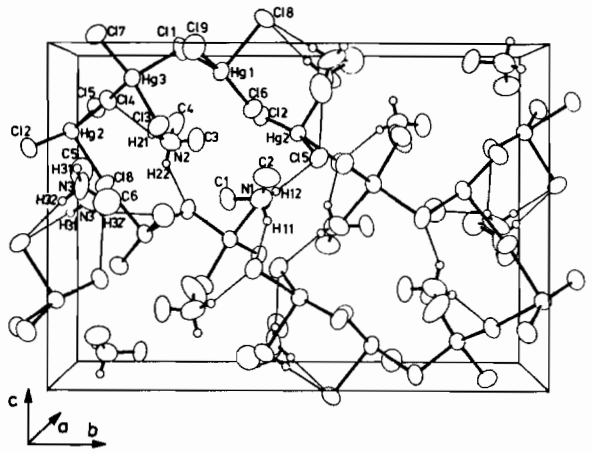

Fig. 1. View of the crystal structure of $(CH_3)_2NH_2HgCl_3$.

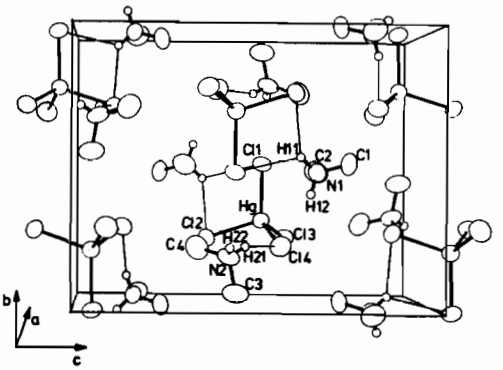

Fig. 2. View of the crystal structure of $\{(CH_3)_2NH_2\}_2$-$HgCl_4$.

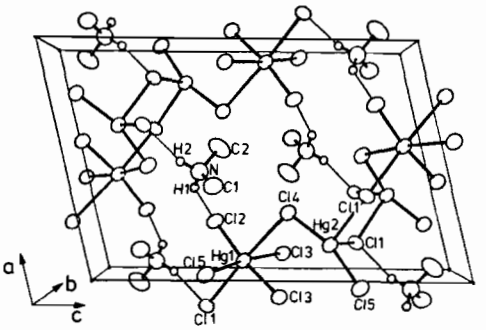

Fig. 3. View of the crystal structure of $(CH_3)_2NH_2Hg_2Cl_5$.

The Hg(II) Coordination

The three independent Hg(II) atoms in the crystal structure of $(CH_3)_2NH_2HgCl_3$ are rather similar. Each Hg atom is involved in four Hg–Cl bonds. Two are short with Hg–Cl distances of 2.33–2.35 Å and involve terminal Cl atoms. The other two are

considerably longer (2.67–2.84 Å) and involve bridging Cl atoms. Fifth and sixth Hg–Cl contacts are found for some of the atoms, but these distances are in the order of 3.37–3.47 Å and are no longer considered to contribute to the bonding. The structure can be considered to consist essentially of discrete $HgCl_2$ units which are, however, considerably distorted by the longer, bridging Hg–Cl contacts. The angles between the short Hg–Cl bonds range from 148 to 158°. This arrangement is rather similar to the crystal structures of $CH_3NH_3HgCl_3$ [7], NH_4HgCl_3 [9] and $NH_4HgCl_3 \cdot H_2O$ [10]. The coordination of the Hg(II) atom in $\{(CH_3)_2NH_2\}_2HgCl_4$ is different. Here a tetrahedral coordination is found. The Hg–Cl distances range from 2.42 to 2.53 Å, while the Cl–Hg–Cl angles range from 102 to 115°. Consequently the tetrahedron is rather heavily distorted. $[HgCl_4]^{2-}$ tetrahedra have also been observed in the crystal structures of $(CH_3NH_3)_2HgCl_4$ [7], $\{(CH_3)_4N\}_2HgCl_4$ [11] and Cs_3HgCl_5 [12]. All these structures deviate from ideal tetrahedra, indicating that the $[HgCl_4]^{2-}$ group is easily distorted by crystal packing effects. The structure of $(CH_3)_2NH_2Hg_2Cl_5$ shows a similarity with the structure of $(CH_3)_2NH_2HgCl_3$. Each Hg atom is again involved in two short Hg–Cl bonds of 2.33–2.35 Å and a number of longer bonds. Hg(1) has four long contacts with Cl atoms ranging from 2.90 to 3.12 Å. Together with the two short bonds they give Hg(1) an octahedral coordination. Hg(2) has only two long bonds. They range from 2.76 to 2.80 Å. Consequently this structure can again be described to consist of discrete $HgCl_2$ units and Cl^- ions where the latter considerably distort the first groups. A similar structure type has been observed for other dimercury pentachlorides: $C_6H_5CH_2NH_3Hg_2Cl_5$ [13] and $CH_3NH_3Hg_2Cl_5$ [7], although for those structures less distorted $HgCl_2$ units were found with short HgCl bonds of 2.29–2.30 Å.

Comparison of the present structures with those of the other mercury(II) chloride complexes studied so far show that the majority of those structures have the distorted octahedral coordination with two short diagonal HgCl bonds and two to four long Hg–Cl bonds. The bond lengths vary however considerably from one compound to the other. A number of compounds has a more or less regular tetrahedral coordination. It can be considered as an extreme limit of the former coordination type.

Only a limited number of compounds has been observed with a trigonal bipyramidal coordination of Hg(II). Typical examples are $(C_2H_5)_4NHgCl_3$ [14], $(CH_3)_3SHgCl_3$ [15] and $S_4N_3HgCl_3$ [16], *i.e.* all mercury trichloride complexes without hydrogen bonding.

Hydrogen Bonding

The dimethylammonium groups are bonded to the Cl atoms via hydrogen bonds. They are tabulated in Table V. The individual hydrogen bonds differ considerably in character. Some are medium-strong bonds (H···Cl distances of 2.3–2.4 Å), while others range from weak to very weak (H···Cl distances 2.7–2.8 Å). The hydrogen bonds in $(CH_3)_2NH_2HgCl_3$ are generally weaker than in the other two compounds. Consequently it is not surprising that one dimethylammonium group in this structure was found to be disordered. Two hydrogen bonds in Table V are bifurcated. They both belong to the very weak interactions.

TABLE V. Hydrogen Bonds.

N–H···Cl	H··Cl [Å]	N···Cl [Å]	N–H–Cl [°]
$(CH_3)_2NH_2HgCl_3$			
N(1)–H(11)···Cl(4)	2.51	3.34(2)	142
N(1)–H(12)···Cl(5)	2.71	3.65(2)	160
N(2)–H(21)···Cl(4)	2.44	3.38(2)	160
N(2)–H(22)···Cl(1)	2.78	3.59(2)	139
N(3)–H(31)···Cl(5)	2.89	3.82(3)	162
N(3)–H(32)···Cl(8)	2.47	3.44(3)	166
N(3')–H(31')···Cl(8)	2.41	3.37(4)	179
N(3')–H(32')···Cl(2)	2.79	3.35(4)	117
N(3')–H(32')···Cl(9)	2.82	3.66(4)	146
$\{(CH_3)_2NH_2\}_2HgCl_4$			
N(1)–H(11)···Cl(1)	2.76	3.34(1)	119
N(1)–H(11)···Cl(2)	2.61	3.35(1)	134
N(1)–H(12)···Cl(3)	2.31	3.25(1)	165
N(2)–H(21)···Cl(4)	2.36	3.23(1)	152
N(2)–H(22)···Cl(2)	2.35	3.24(1)	155
$(CH_3)_2NH_2Hg_2Cl_5$			
N–H(1)···Cl(2)	2.44	3.28(1)	144
N–H(2)···Cl(1)	2.28	3.21(1)	164

Acknowledgement

One of us (ABS) gratefully acknowledges financial support of the Deutscher Akademischer Austauschdienst and of the Gesellschaft für Technische Zusammenarbeit.

References

1 H. Mashiyama, *J. Phys. Soc. Japan, 49*, 2270 (1980).
2 C. Dupas and J. P. Renard, *Phys. Lett., 43A*, 119 (1973). R. J. Birgeneau, G. Shirane and T. A. Kitchens, *Low Temp. Phys., 13*, 371 (1974).
3 V. Subramanian and K. Seff, *Acta Crystallogr., B36*, 2132 (1980).

4 M. Sandström, *Thesis,* Stockholm (Sweden), 1978.
5 R. Hoppe, V. Wilhelm and B. Müller, *Z. anorg. allg. Chem., 392,* 1 (1972).
6 D. Grdenič, *Quart. Rev. (London), 19,* 303 (1965).
7 A. Ben Salah, J. W. Bats, R. Kalus, H. Fuess and A. Daoud, *Z. anorg. allg. Chem.,* in press.
8 A. Ben Salah, *Thesis,* Institut National Polytechnique de Toulouse (France) 1979.
9 E. J. Harmsen, *Z.f. Kristallogr., 100,* 208 (1938).
10 K. Sagisawa, K. Kitahama, H. Kiriyama and R. Kiriyama, *Acta Crystallogr., B30,* 1603 (1974).
11 B. Kamenar and A. Nagl, *Acta Crystallogr., B32,* 1414 (1976).
12 W. Clegg, M. L. Brown and L. J. A. Wilson, *Acta Crystallogr., B32,* 2905 (1976).
13 J. W. Bats, H. Fuess and A. Daoud, *Acta Crystallogr., B36,* 2150 (1980).
14 M. Sandström and D. H. Liem, *Acta Chem. Scand., A32,* 509 (1978).
15 P. Biscarini, L. Fusina, G. Nivellini and G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* 664 (1977).
16 K. Weidenhammer and M. L. Ziegler, *Z. anorg. allg. Chem., 434,* 152 (1977).