Acta Chemica Scandinavica A 32 (1978) 509–514

Crystal Structure of α-Tetraethylammonium Trichloromercurate(II)

MAGNUS SANDSTRÖM and DJIET HAY LIEM

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

The structure of the compound $[N(C_2H_5)_4]HgCl_3$ was determined from three-dimensional single-crystal X-ray diffraction data collected at room temperature on an automatic Syntex $P2_1$ four-circle diffractometer. The unit cell is triclinic, space group $P\bar{1}$, with $a=7.644(1)$, $b=9.749(2)$, $c=10.325(2)$ Å, $\alpha=62.78(1)$, $\beta=86.91(1)$, $\gamma=86.07(1)°$, and $Z=2$. The structure, refined to a final conventional R value of 0.039, comprises planar trigonal $HgCl_3^-$ anions and NEt_4^+ cations of almost regular S_4 symmetry. The average Hg–Cl bond length is 2.43 Å. Two long Hg–Cl contacts at 3.054(3) and 3.017(3) Å complete a trigonal bipyramidal configuration around Hg and bridge adjacent $HgCl_3^-$ ions, giving rise to infinite chains parallel to the x axis. A comparison is made with other structures where mercury(II) is surrounded by halide ions in a trigonal bipyramidal configuration. A probable structure change is proposed for the transition from the α to the β form of $[NEt_4]HgCl_3$.

Crystal structure determinations of trihalidomercurate(II) salts show a variety of different mercury(II) coordinations.[1] Planar trigonal coordination occurs for several compounds containing HgX_3^- ions (X=I, Br and Cl), where two long Hg–X interactions complete a trigonal bipyramidal configuration.[2-7]

Tetrahedral coordination in chains of HgX_4 tetrahedra sharing two apexes is found in several compounds.[8-13] Distorted tetrahedral coordination also occurs in the discrete dimeric $Hg_2X_6^{2-}$ complexes with X=I[14] or Br[15,16] where two tetrahedra share an edge.

For several trichloromercurate(II) salts distorted octahedral coordination with two short digonal Hg–Cl bonds, is found. These octahedra can share apexes to form sheets[17,18] or a distorted perovskite structure as in $CsHgCl_3$,[19,20] or edges to give a double-rutile chain structure.[21-22]

By X-ray diffraction methods the HgI_3^- and $HgBr_3^-$ ions are found to be pyramidal in aqueous and dimethyl sulfoxide (DMSO) solutions. Coordinated solvent molecules probably complete a tetrahedral coordination (for $HgBr_3^-$ in DMSO possibly distorted trigonal bipyramidal).[23-25]

In concentrated aqueous solutions with the mol ratio Cl/Hg≈3 polymeric Hg–Cl complexes occur, probably with the distorted octahedral coordination mentioned above.[26] In DMSO solutions, however, monomeric $HgCl_3^-$ ions are found with an average Hg–Cl bond length of 2.434(4) Å.[25] The X-ray diffraction and Raman data are consistent with a planar trigonal structure with two DMSO oxygen atoms completing a trigonal bipyramidal coordination.[25] Since spectroscopic data indicated the compound α-$[NEt_4]HgCl_3$ to contain discrete $HgCl_3^-$ ions,[13] its structure was determined in the present work to provide a comparison with the solution data.

EXPERIMENTAL

Colourless crystals of α-$[NEt_4]HgCl_3$ were prepared as described previously.[13] The compound was identified by its strong ν_1(Hg–Cl) Raman line at 269 cm^{-1}.[13] Its density, $D_m=2.10(2)$, was determined by the apparent loss of weight in benzene.

The X-ray data were obtained using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) at room temperature on a prismatic crystal with a largest dimension of about 0.15 mm. The unit cell parameters were determined by the standard procedure on the computer-controlled Syntex $P2_1$ four-circle diffractometer,[27] and refined by least-squares methods for 25 centred reflections, all with $2\theta>30°$. A triclinic unit cell was found with $a=7.644(1)$, $b=9.749(2)$, $c=10.325(2)$ Å. $\alpha=62.78(1)$, $\beta=86.91(1)$, $\gamma=86.07(1)°$, $V=682.5(2)$ Å^3, and $D_x=2.128$ for $Z=2$.

The ω scan technique with variable scan speeds from 0.5° min^{-1} upwards was used. Four check reflections were measured regularly every 100th reflection. All their intensities increased continuously, but markedly more for the strong low-angle reflections, indicating extinction changes. The largest increase, 27 %, was obtained for the 011 check reflection. Of the 2396 possible independent hkl, $h\bar{k}l$, $hk\bar{l}$ and $h\bar{k}\bar{l}$ reflections measured for $2\theta < 50°$, 2183 reflections had intensities larger than $1.96\sigma(I)$ and were considered observed.

A semi-empirical absorption correction method was applied on the data, as described previously.[27] The largest variation obtained in the relative intensity correction factors was from 1 to 0.63. The linear absorption coefficient μ(Mo$K\alpha$) is 121 cm^{-1}.

Further data reduction to scaled $|F_o|$ values was performed as previously, using computer programs and scattering factors from the same sources.[27] Anomalous dispersion corrections were included for the Hg and Cl atoms.

STRUCTURE DETERMINATION AND REFINEMENT

From a three-dimensional Patterson peak listing, centrosymmetrical positions of the two Hg and six Cl atoms of the unit cell could be deduced, consistent with the space group $P\bar{1}$ (No. 2). Full-matrix least-squares refinements of these initial parameters using isotropic temperature factors yielded a conventional R value of 0.15 and weighted R_w of 0.22, defined as before.[27] A difference Fourier synthesis revealed the positions of all non-H atoms and refinements with the Hg and Cl atoms anisotropic gave $R = 0.040$ and $R_w = 0.066$. Refinements with all atoms anisotropic further decreased R to 0.039 and R_w to 0.062, which is a significant improvement according to the Hamilton test.[28] A total of 118 parameters was refined. The parameter shifts in the last refinement cycle were all less than 1 % of the corresponding standard deviation. The highest of the peaks in a final difference Fourier map was 0.92 e $Å^{-3}$. Only a few of these peaks corresponded to any of the 20 possible H atom positions. Therefore, no H atoms were included in the final model.

The final parameter values are given in Tables 1 and 2.

The function minimized in the least-squares refinement was $\Sigma w\|F_o| - |F_c\|^2$. The weighting function w was chosen as $w = 1/\{\sigma^2(F_o) + (0.04F_o)^2\}$. This gave a satisfactory weighting scheme according to statistical analyses of the error distribution, except for some of the weakest reflections indicating systematic errors in this part of the measured data. All 119 reflections with $|F_o| < 10$ have therefore been omitted in the refinements reported here, which caused a decrease in the final R value from 0.041 to 0.039.

DISCUSSION

General. The structure comprises planar trigonal $HgCl_3^-$ anions, stacked in columns parallel to the x axis and surrounded by discrete $[N(C_2H_5)_4]^+$ cations (Figs. 1 and 2). Some interatomic distances and angles are given in Table 3.

The $HgCl_3^-$ ion. The average Hg–Cl bond length in the planar $HgCl_3^-$ unit is 2.43_2 Å. The deviations

Table 1. Final fractional atomic positional parameters with estimated standard deviations in parentheses.

Atom	x	y	z
Hg	0.25071(5)	0.04711(5)	0.42529(4)
Cl1	0.2609(4)	0.2006(4)	0.1601(3)
Cl2	0.0598(4)	0.1372(4)	0.5694(4)
Cl3	0.4324(4)	−0.1900(3)	0.5328(4)
N	0.2334(10)	0.6633(9)	0.1679(9)
C1	0.2945(15)	0.8083(12)	0.1739(13)
C2	0.4893(17)	0.8184(14)	0.1708(13)
C3	0.3013(16)	0.6503(17)	0.0320(14)
C4	0.2404(19)	0.7827(18)	0.8899(13)
C5	0.3097(15)	0.5247(12)	0.2946(13)
C6	0.2571(14)	0.5095(14)	0.4445(11)
C7	0.0341(14)	0.6727(16)	0.1757(13)
C8	0.0526(17)	0.4655(15)	0.8097(15)

Table 2. Final anisotropic thermal parameters (Å^2) with estimated standard deviations in parentheses. The expression used for the temperature factor is $\exp[-1/4(B_{11}h^2a^*+\cdots+2B_{12}hka^*b^*+\cdots)]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	3.93(2)	3.32(2)	2.88(2)	0.50(1)	0.21(1)	−1.30(2)
Cl1	4.23(11)	4.52(13)	2.81(11)	−0.30(10)	0.07(9)	−1.51(10)
Cl2	3.78(11)	4.42(13)	5.65(15)	−0.82(10)	1.45(10)	−3.42(12)
Cl3	3.94(11)	3.32(11)	5.24(14)	0.85(9)	−1.28(10)	−2.49(11)
N	3.0(3)	2.6(3)	2.6(3)	−0.4(3)	0.4(3)	−1.5(3)
C1	4.9(5)	2.3(4)	4.2(5)	−0.6(4)	0.1(4)	−2.1(4)
C2	5.2(6)	4.1(5)	3.2(5)	−1.3(5)	0.9(4)	−1.2(4)
C3	4.1(5)	6.4(7)	3.6(5)	−0.7(5)	1.3(4)	−3.2(5)
C4	6.4(7)	7.2(8)	1.8(4)	−0.3(6)	−0.4(4)	−2.2(5)
C5	3.9(5)	3.0(4)	3.6(5)	0.6(4)	−0.8(4)	−1.3(4)
C6	4.1(5)	4.3(5)	2.2(4)	−0.9(4)	0.0(4)	−0.8(4)
C7	2.6(4)	6.0(6)	4.0(5)	0.4(4)	−0.5(4)	−2.8(5)
C8	4.5(6)	4.3(6)	4.4(6)	−0.9(5)	0.4(5)	−0.9(5)

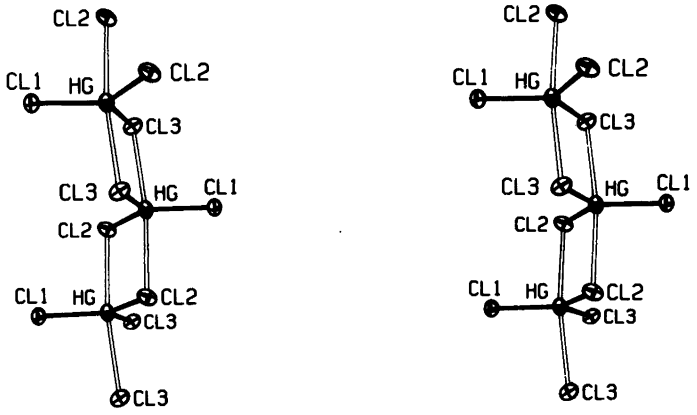

Fig. 1. A stereoscopic view of the chain of $HgCl_3^-$ anions. The long bridging interactions are shown by the unfilled bonds. The thermal ellipsoids include 30 % probability.

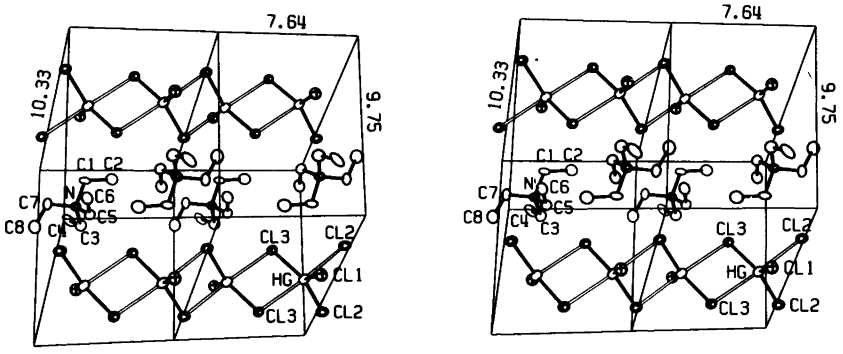

Fig. 2. A stereoscopic illustration of the molecular packing viewed almost perpendicular to the *b* edge. The cell edges of two unit cells are outlined with their lengths in Å. The thermal ellipsoids enclose 30 % probability. The long Hg−Cl bridging interactions are shown by the unfilled bonds.

Table 3. Some interatomic distances (Å) and bond angles (°). Estimated standard deviations are given in parentheses. The superscripts imply the following symmetry operations relative to *x*, *y*, *z* in Table 1: [a] $\bar{x}$, $\bar{y}$, 1-*z* and [b] 1-*x*, $\bar{y}$, 1-*z*.

Hg–Cl1	2.444(3)	Cl1–Hg–Cl2	118.9(1)
Hg–Cl2	2.426(3)	Cl1–Hg–Cl3	118.3(1)
Hg–Cl3	2.426(3)	Cl2–Hg–Cl3	122.9(1)
Hg–Cl2[a]	3.054(3)	Cl2[a]–Hg–Cl3[b]	171.1(1)
Hg–Cl3[b]	3.017(3)	Cl1–Hg–Cl2[a]	94.9(1)
Hg–Hg[a]	4.050(1)	Cl1–Hg–Cl3[b]	93.6(1)
Hg–Hg[b]	4.070(1)	Cl2–Hg–Cl2[a]	85.4(1)
N–C1	1.546(16)	Cl2–Hg–Cl3[b]	92.9(1)
N–C3	1.524(16)	Cl3–Hg–Cl2[a]	89.8(1)
N–C5	1.494(15)	Cl3–Hg–Cl3[b]	83.8(1)
N–C7	1.518(13)	C1–N–C3	113.0(9)
C1–C2	1.495(18)	C1–N–C5	107.7(8)
C3–C4	1.514(19)	C1–N–C7	106.5(8)
C5–C6	1.518(16)	C3–N–C5	106.0(9)
C7–C8	1.483(22)	C3–N–C7	111.3(9)
		C5–N–C7	112.3(9)
		N–C1–C2	114.6(10)
		N–C3–C4	114.4(11)
		N–C5–C6	116.0(10)
		N–C7–C8	115.6(11)

from a weighted least-squares plane are for Hg −0.0001(4) Å, for Cl1, Cl2 and Cl3 0.002(3) Å. Two long Hg–Cl interactions at 3.054(3) and 3.017(3) Å to the adjacent $HgCl_3^-$ ions complete a slightly distorted trigonal bipyramidal configuration (the sum of the van der Waals radii of Hg[29] and Cl is 3.3_0 Å), where the bipyramids share two of their long edges on opposite sides (Figs. 1 and 3). These bridging chlorine atoms form asymmetric double bridges between the Hg atoms giving rise to infinite $(HgCl_3^-)_n$ chains (Fig. 2).

Comparison with other trigonal bipyramidal Hg–X configurations. The same type of chain as in the present structure has been found in the compounds $Hg_3I_6(en)_2$ where en = ethylenediamine, $C_2H_8N_2$,[4] in $[S(CH_3)_3]HgI_3$,[2] and recently in $[S(CH_3)_3]HgCl_3$,[6] where the average bond length in the trigonal $HgCl_3^-$ unit is 2.42_7 Å and the long Hg–Cl interactions 3.040(5) and 3.049(5) Å. The $(HgBr_3^-)_n$ chain in $[N(CH_3)_4]HgBr_3$ can also be described in this way even though the Hg atoms are all displaced approximately 0.3 Å above the plane through the bromine atoms in the $HgBr_3^-$ units,[11] thus giving a pseudotetrahedral coordination intermediate to the chains of HgX_4-tetrahedra sharing two apexes (*cf.* Fig. 3) found in, *e.g.*, $KHgBr_3.H_2O$,[10] $KHgI_3.H_2O$[9] and $[N(CH_3)_4]HgI_3$.[8]

Neither in the vibrational spectra of the compounds $[S(CH_3)_3]HgCl_3$,[6] α-$[NEt_4]HgCl_3$ and $[S(CH_3)_3]HgI_3$,[13] with the bipyramidal arrangement described above (*cf.* Fig. 3), nor in that of $[N(CH_3)_4]HgBr_3$,[13] were bridging Hg–X modes found, implying that the long Hg–X interactions are quite weak. However, infrared bands which can be assigned to bridging frequencies occur in the spectrum of $[N(CH_3)_4]HgI_3$,[13] consistent with the structure reported for this compound.[8] Similar bridging frequencies are also found[13] in the spectrum of the high-temperature form, β-$[NEt_4]HgCl_3$, of the compound studied in the present work. Consequently, it seems probable that the same type of apex-sharing chains of HgX_4-tetrahedra[8] occur in these compounds, and thus that the α to β transition of $[NEt_4]HgCl_3$ consists only of a displacement of the Hg atoms approximately 0.4 Å perpendicular to the plane through the chlorine atoms in the $HgCl_3^-$ unit (Fig. 3).

The bipyramidal chain type discussed above leaves only one non-bridging halogen atom in each HgX_3^- unit. Another arrangement, giving two non-bridging halogen atoms, is found in the $(HgCl_3^-)_n$ chain in $[S_4N_3]HgCl_3$ (*cf.* Ref. 7, Fig. 2). One of the chlorine atoms of each planar $HgCl_3^-$ unit has two long interactions, 3.022(8) and 3.204(9)

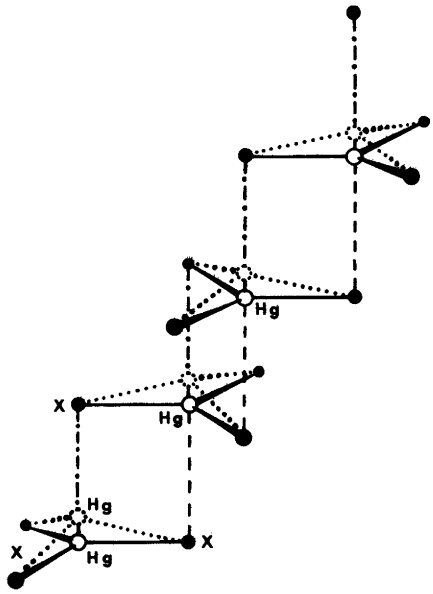

Fig. 3. A perspective view showing the probable structure change of the $(HgCl_3^-)_n$ chain due to a displacement of the mercury atoms (open circles) at the α to β transition of $[N(C_2H_5)_4]HgCl_3$. The solid and dashed lines show the the bipyramidal arrangement in the α form. The lines with dots visualize the chain of $HgCl_4$ tetrahedra sharing two apexes which probably occur in β-$[N(C_2H_5)_4]HgCl_3$. The same types of coordination occur in several other HgX_3 compounds (see text).

Å, to the Hg atoms of the adjacent $HgCl_3^-$ ions thus forming a double-chain of bipyramids on top of each other, fused by sharing the two long edges on the same side of each bipyramid. The average Hg–Cl bond length in the $HgCl_3^-$ unit is 2.42_3 Å.[7]

There seems to be no correlation between the short Hg–X bond lengths for bridging and non-bridging halogen atoms in either of the two chain types, which is an additional indication of the weakness of these bridging interactions.

Columns of HgX_3^- ions joined by interjacent equidistant halide ions, thus forming single chains of apex-sharing bipyramids on top of each other with all the three halogen atoms of HgX_3^- non-bridging, are found in the compounds Hg_2NHBr_2 [5] and $K_2HgI_4.3H_2O$ [3] (*cf.* Ref. 1, Fig. 1).

Discrete regular trigonal bipyramidal $HgCl_5^{3-}$ complex ions also occur, but have shorter axial, 2.518(4) Å, than equatorial, 2.640(4) Å, bond lengths.[30] The ratio is 0.954(3) which can be compared with the corresponding ratios ranging between 1.25 and 1.33 for the bipyramidal configurations in the $(HgX_3^-)_n$ chains.

The $[N(C_2H_5)_4]^+$ ion. The tetraethylammonium ion is well-ordered and has an almost regular S_4 symmetry (*cf.* Fig. 2 and Table 3). The deviations from the two almost perpendicular (87.8°) planes through the N atom and the C atoms of the opposite ethyl groups are less than 0.011 Å (which is less than 1σ) for all atoms except C8 (deviation 0.187(14) Å). The ethyl groups are in contact with the Cl atoms of the $HgCl_3^-$ ions. The closest approach is C5–Cl3, 3.45(1) Å, which is slightly shorter than the sum of the van der Waals radii, 3.6 Å.[31]

The average bond lengths found, C–N 1.52(2) Å and C–C 1.50(2) Å, are in good agreement with average values reported in a recent precise determination, C–N 1.528(3) Å and C–C 1.504(13) Å.[32]

Acknowledgements. The authors wish to thank the Swedish Natural Science Research Council and the foundation "Knut & Alice Wallenbergs Stiftelse" for economic support. Professor Ingmar Grenthe, Dr. Georg Johansson and Mr. Ivaylo Toromanov are gratefully thanked for their interest in this work.

REFERENCES

1. Sandström, M. *Thesis*, Royal Institute of Technology, Stockholm 1978. (Available on request).
2. Fenn, R. H. *Acta Crystallogr. 20* (1966) 20.
3. Gerken, V. A. and Pakhomov, V. I. *Zh. Strukt. Khim. 10* (1969) 753.
4. Grdenić, D., Sikirica, M. and Vicković, I. *Acta Crystallogr. B 33* (1977) 1630.
5. Brodersen, K. *Acta Crystallogr. 8* (1955) 723.
6. Biscarini, P., Fusina, L., Nivellini, G. and Pelizzi, G. *J. Chem. Soc. Dalton Trans.* (1977) 664.
7. Weidenhammer, K. and Ziegler, M. L. *Z. Anorg. Allg. Chem. 434* (1977) 152.
8. Fedorov, P. M. and Pakhomov, V. I. *Koord. Khim. 1* (1975) 1140.
9. Nyqvist, L. and Johansson, G. *Acta Chem. Scand. 25* (1971) 1615.
10. Padmanabhan, V. M. and Yadava, V. S. *Acta Crystallogr. B 25* (1969) 647.
11. White, J. G. *Acta Crystallogr. 16* (1963) 397.
12. Herlinger, A. H. *Spectrosc. Lett. 8* (1975) 787.
13. Barr, R. M. and Goldstein, M. *J. Chem. Soc. Dalton Trans.* (1976) 1593, and references therein.

14. Beurskens, P. T., Bosman, W. P. J. H. and Cras, J. A. *J. Cryst. Mol. Struct. 2* (1972) 183.
15. Harris, G. S., Inglis, F., McKechnie, J., Cheung, K. K. and Ferguson, G. *Chem. Commun. 9* (1967) 442.
16. Gal, A. W., Beurskens, G., Cras, J. A., Beurskens, P. T. and Willemse, J. *Recl. Trav. Chim. Pays-Bas 95* (1976) 157.
17. Harmsen, E. J. *Z. Kristallogr. 100* (1938) 208.
18. Barr, R. M. and Goldstein, M. *J. Chem. Soc. Dalton Trans.* (1974) 1180.
19. Zvonkova, Z. V., Samodurova, V. V. and Vorontsova, L. G. *Dokl. Akad. Nauk. SSSR 102* (1955) 1115.
20. Scaife, D. E. *Aust. J. Chem. 24* (1971) 1753.
21. Sagisawa, K., Kitahama, K., Kiriyama, H. and Kiriyama, R. *Acta Crystallogr. B 30* (1974) 1603, and references therein.
22. Authier-Martin, M. and Beauchamp, A. L. *Can. J. Chem. 53* (1975) 2345.
23. Gaizer, F. and Johansson, G. *Acta Chem. Scand. 22* (1968) 3013.
24. Sandström, M. and Johansson, G. *Acta Chem. Scand. A 31* (1977) 132.
25. Sandström, M. *Acta Chem. Scand. A 32* (1978). *In press.*
26. Sandström, M. *Acta Chem. Scand. A 31* (1977) 141.
27. Sandström, M. and Persson, I. *Acta Chem. Scand. A 32* (1978) 95, and references therein.
28. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1968 and 1974, Vols. 3 and 4.
29. Grdenić, D. *Q. Rev. Chem. Soc. 19* (1965) 303.
30. Clegg, W., Greenhalgh, D. A. and Straughan, B. F. *J. Chem. Soc. Dalton Trans.* (1975) 2591.
31. Harmon, K. M., Gennick, I. and Madeira, S. L. *J. Phys. Chem. 78* (1974) 2585, and references therein.
32. Elder, R. C. and Pesa, F. *Acta Crystallogr. B 34* (1978) 268.

Received February 13, 1978.