Crystal Structure of Hexakis(pyridine 1-oxide)mercury(II) Bisperchlorate

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The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction by use of conventional heavy-atom methods. The structure was refined by a block-diagonal least-squares procedure to *R* 0·08 for 345 independent visually estimated reflections. Crystals are rhombohedral, space group $R\bar{3}$, $a = 9{\cdot}77 \pm 0{\cdot}01$ Å, $\alpha = 80{\cdot}7 \pm 0{\cdot}1°$ (hexagonal cell: $a = 12{\cdot}64$, $c = 19{\cdot}47$ Å), $Z = 1$.

The structure consists of cubic close-packed layers of $[Hg(C_5H_5NO)_6]^{2+}$ cations with the ClO_4^- ions in ' trigonal holes ' of the array. The mercury has regular octahedral co-ordination, *d*(Hg–O) 2·35 Å. Distances and angles within the ligand and the perchlorate ion are as expected. The i.r. spectrum of the perchlorate ion shows band-splitting consistent with its C_{3v} symmetry.

THE most common co-ordination configuration of mercury is that of a distorted octahedron, with two short digonal bonds and four weaker bonds in the perpendicular plane.[1,2] There have been several reports of monomeric six-co-ordinate mercury(II) species,[3-6] but the only structural evidence available is for $[Hg(SCN)_2(o\text{-}phen)_2]$ (*o*-phen = 1,10-phenanthroline) in which the mercury environment is a distorted octahedron.[6] Octahedral mercury co-ordination was suggested for the compound $[Hg(C_5H_5NO)_6](ClO_4)_2$ on the basis of the similarity of the *X*-ray powder pattern with those of the nickel and cobalt analogues,[4] although no conclusion was reached as to the presence or absence of distortion in the octahedron. Since there appears to be only one ligand type, the structure of $[Hg(C_5H_5NO)_6](ClO_4)_2$ was determined in order to reveal the preferred stereochemistry for six-co-ordinate mercury(II).

EXPERIMENTAL AND RESULTS

The complex was prepared by the method of ref. 4, and recrystallised from absolute methanol (m.p. 170—171 °C, lit.[7] 168—169 °C) as small rhombs.

The i.r. spectra (1300—500 cm^{-1}) of the complex and of the pyridine 1-oxide ligand were measured as Nujol mulls between KBr plates by use of a Perkin-Elmer 337 spectrophotometer with a Polystyrene reference. The absorption frequencies (cm^{-1}) and intensities (s, strong; m, medium; w, weak; v, very; b, broad) of the mercury complex were: 1240vs, 1171s, 1127vs, 1077vs, 1015s, 938w, 909w,b, 835s, 752s, 670s, 629s, 621m, 546m, and 508w.

Crystallography.—A crystal closely approximating a cube of edge 0·07 mm was used. A preliminary Weissenberg investigation showed the crystal system to be rhombohedral and this unit cell and symmetry were used for the structural analysis. Non-integrated *X*-ray data were collected at room temperature by the multiple-film equi-inclination Weissenberg technique. The crystal was mounted about the rhombohedral axis (*a*) and the layers 0—4*kl* recorded. Unit-cell calibration was effected by superimposing aluminium powder lines ($a_{298\,K}$ 4·0494 Å)[8] on a zero-layer photograph. Nickel-filtered copper radiation [$\lambda(K_{\bar{\alpha}})$, 1·5418 Å][9] was used throughout.

Crystal Data.—$C_{30}H_{30}Cl_2HgN_6O_{14}$, $M = 970{\cdot}1$, Rhombohedral, $a = 9{\cdot}77 \pm 0{\cdot}01$ Å, $\alpha = 80{\cdot}7 \pm 0{\cdot}1°$, $U = 898$ Å^3, (hexagonal unit cell, $a = 12{\cdot}64$, $c = 19{\cdot}47$ Å), $D_m = 1{\cdot}80$ (flotation), $Z = 1$, $D_c = 1{\cdot}79$, $F(000) = 478$. Space group $R\bar{3}$ (No. 148, C_{3i}^2).[10] $\mu(\text{Cu-}K_{\bar{\alpha}}) = 103$ cm^{-1}; transmission coefficient range 0·277—0·350.

Intensities were estimated visually by use of a calibrated intensity strip, only non-zero reflections being included in the data. Data were corrected for absorption[11] and from the original data set (*hkl*), a second symmetry-related set (*lhk*) was generated which included only data common to the first set. By this means, scaling by internal correlation[12] was effected after both sets of data had been corrected for Lorentz and polarisation factors. A unique data set (345 reflections) was then selected, averaging the structure factor amplitudes of symmetry-related reflections.

Structure Determination.—Examination of Weissenberg photographs taken with the crystal rotated about the three-fold axis revealed the Laue symmetry to be $\bar{3}$. Of the two possible space groups $R\bar{3}$ and $R3$, the centrosymmetric space group $R\bar{3}$ was chosen and apparently vindicated by the successful structural analysis; the other possibility ($R3$) was not pursued further. Since $Z = 1$, the mercury atom must have site-symmetry $\bar{3}$ and be located at the origin. A structure-factor calculation with the mercury atom assigned an isotropic thermal parameter *B* 3·0 Å^2 gave a conventional residual *R* 0·36. Subsequent difference-Fourier syntheses revealed the remainder of the non-hydrogen atoms in general positions, except for the chlorine atom and one of the oxygen atoms of the perchlorate located on the three-fold axis. The positional and isotropic thermal parameters of all atoms were then refined by a block-diagonal (3 × 3, 6 × 6) least-squares procedure (local program SFLS1,2 by A. I. M. Rae), minimising the function $\Sigma w(|F_o| - |F_c|)^2$, to *R* 0·121 and *R′* 0·143 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. An anisotropic temperature factor of the form: $\exp-[h^2\beta_{11} + hk\beta_{12} + hl\beta_{13} + k^2\beta_{22} + kl\beta_{23} + l^2\beta_{33}]$ was introduced for the mercury atom; of the six components, only β_{11} and β_{12} are independent for the $\bar{3}$ site-

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symmetry ($\beta_{11} = \beta_{22} = \beta_{33}$, $\beta_{12} = \beta_{13} = \beta_{23}$).[13] A weighting scheme $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced and found appropriate,[14] the constants a and b being redetermined as refinement proceeded. The refinement converged at a final R of 0·084 (R' 0·110), all parameter shifts being <0·25σ. A final difference-Fourier synthesis was substantially flat, the largest peak being of the order of <0·3 of a carbon atom. Final weighting scheme constants were a = 14·27 and b = 0·0175.

TABLE 1

Final atomic fractional cell parameters and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Hg	0 *	0 *	0 *	†
Cl	0·351(2)	0·351(2)	0·351(2)	5·6(2)
O(11)	0·424(6)	0·424(6)	0·424(6)	10·9(11)
O(12)	0·344(2)	0·221(2)	0·431(3)	11·2(7)
O(1)	0·020(2)	−0·048(2)	0·240(2)	5·2(3)
N(1)	−0·049(2)	0·050(2)	0·314(2)	4·8(4)
C(2)	−0·189(3)	0·050(3)	0·341(3)	7·1(7)
C(3)	−0·267(3)	0·162(3)	0·419(3)	7·5(7)
C(4)	−0·197(3)	0·246(3)	0·479(3)	7·6(7)
C(5)	−0·050(3)	0·234(3)	0·447(3)	7·8(7)
C(6)	0·019(3)	0·135(3)	0·368(3)	6·1(6)

* Special position. † Anisotropic thermal parameters (× 10^4) for the mercury atom (see text): β_{11} 137(5), β_{12} −58(8).

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) HgO$_6$ octahedron

Hg$^{\rm I}$–O(1$^{\rm I-VI}$)	2·35(2)	O(1$^{\rm I}$)–Hg$^{\rm I}$–O(1$^{\rm II}$)	89·3(5)
O(1$^{\rm I}$) · · · O(1$^{\rm II,III}$)	3·30(2)	O(1$^{\rm I}$)–Hg$^{\rm I}$–O(1$^{\rm V}$)	90·7(5)
O(1$^{\rm I}$) · · · O(1$^{\rm V,VI}$)	3·34(2)	Hg$^{\rm I}$–O(1$^{\rm I}$)–N(1$^{\rm I}$)	114·3(12)

(b) Pyridine 1-oxide ligand

O(1)–N(1)	1·32(2)	O(1)–N(1)–C(2)	115(2)
N(1)–C(2)	1·35(4)	O(1)–N(1)–C(6)	122(2)
N(1)–C(6)	1·36(3)	C(2)–N(1)–C(6)	123(2)
C(2)–C(3)	1·48(4)	N(1)–C(2)–C(3)	115(2)
C(3)–C(4)	1·39(5)	C(2)–C(3)–C(4)	121(3)
C(4)–C(5)	1·41(5)	C(3)–C(4)–C(5)	118(3)
C(5)–C(6)	1·36(4)	C(4)–C(5)–C(6)	119(3)
		C(5)–C(6)–N(1)	122(2)

(c) Perchlorate ion

Cl$^{\rm I}$–O(11$^{\rm I}$)	1·42(6)
Cl$^{\rm I}$–O(12$^{\rm I,II,III}$)	1·38(3)
O(11$^{\rm I}$)–O(12$^{\rm I}$)	2·23(7)
O(12$^{\rm I}$)–O(12$^{\rm II,III}$)	2·31(4)
O(11$^{\rm I}$)–Cl$^{\rm I}$–O(12$^{\rm I,II,III}$)	105(3)
O(12$^{\rm I}$)–Cl$^{\rm I}$–O(12$^{\rm II,III}$)	113(2)

(d) Intermolecular contacts <3·5 Å

O(11$^{\rm I}$) · · · O(11$^{\rm VII}$)	2·97(9)	O(1$^{\rm I}$) · · · N(1$^{\rm II}$)	3·16(2)
O(12$^{\rm I}$) · · · C(5$^{\rm II}$)	3·45(4)	N(1$^{\rm I}$) · · · C(5$^{\rm VIII}$)	3·44(4)
O(1) · · · C(5$^{\rm VIII}$)	3·33(3)	N(1) · · · C(6$^{\rm VIII}$)	3·36(3)
O(1$^{\rm I}$) · · · C(2$^{\rm VI}$)	3·18(3)	C(6$^{\rm I}$) · · · C(6$^{\rm VIII}$)	3·39(4)

Transformations of the asymmetric unit (x, y, z) are defined by Roman numeral superscripts. No superscript implies I.

I	x, y, z	V	$\bar{z}, \bar{x}, \bar{y}$
II	z, x, y	VI	$\bar{y}, \bar{z}, \bar{x}$
III	y, z, x	VII	$1 - x, 1 - y, 1 - z$
IV	$\bar{x}, \bar{y}, \bar{z}$	VIII	$\bar{x}, \bar{y}, 1 - z$

TABLE 3

Equations of least-squares planes in the form $lX + mY + nZ = p$, referred to an orthogonal frame (X, Y, Z) derived from the rhombohedral unit cell by the transformation:

$$[X, Y, Z] = \begin{bmatrix} a & b\,.\cos\alpha & c\,.\cos\alpha \\ 0 & b\,.\sin\alpha & c\,.\cos\alpha\,(1 - \cos\alpha) \\ 0 & 0 & U/a^2\,.\sin\alpha \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Atomic deviations (Å) and standard deviations (σ Å) are given

	l	m	n	p	σ
Plane (1):					
N(1), C(2)—(6)	0·099	−0·554	0·827	2·007	0·03

[N(1) −0·02, C(2) 0·04, C(3) −0·04, C(4) 0·03, C(5) 0·00, C(6) 0·00, O(1) 0·01, Hg −2·01]

	l	m	n	p	σ
Plane (2):					
Hg, O(1), N(1)	0·881	0·445	−0·163	0·000	0·00

Angle between normals to planes (1) and (2) 72·9°

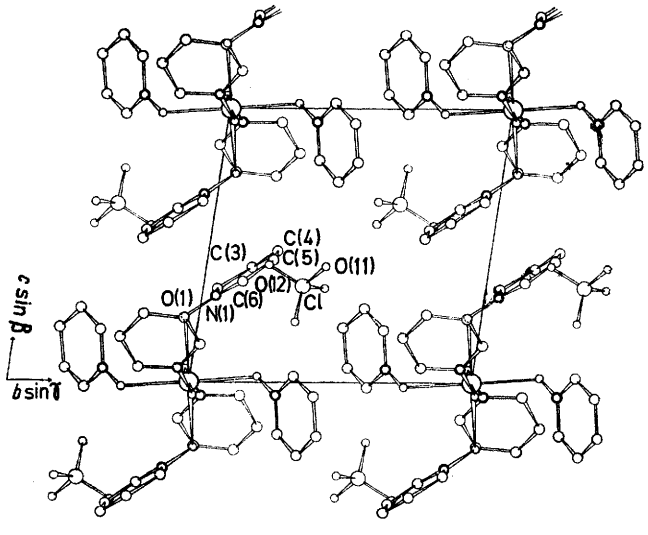

FIGURE 1 Projection of the rhombohedral cell on [100], giving atomic numbering

Atomic scattering factors used were for divalent mercury,[15] corrected for anomalous dispersion (Δf', Δf'')[16] and for neutral chlorine, oxygen, nitrogen, and carbon.[15] The final set of observed and calculated structure factors is given in a Supplementary Publication No. SUP 206303 (3 pp., 1 microfiche).* Final atomic positional and thermal parameters are given in Table 1 together with least-squares estimated standard deviations, which are likely to be underestimates in view of the block-diagonal refinement procedure. Interatomic distances and angles[17] are given in Table 2 and least-squares planes in Table 3. The unit cell contents are depicted in Figure 1, together with the atomic

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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numbering system. Figure 2 gives views of the [Hg(C$_5$H$_5$NO)$_6$]$^{2+}$ cation parallel and perpendicular to the three-fold axis.

Calculations were performed on a DEC PDP 10 computer at the University of Western Australia.

DISCUSSION

The structure consists of cubic close-packed layers of [Hg(C$_5$H$_5$NO)$_6$]$^{2+}$ cations with the perchlorate ions located in ' trigonal holes ' of the array; both cations and anions are centred on the three-fold axes. The closest approach of the mercury atoms is the axial length of 9·77 Å. The cations pack so that adjacent pyridine rings of neighbouring cations are parallel, the shortest contacts being *ca.* 3·3 Å.

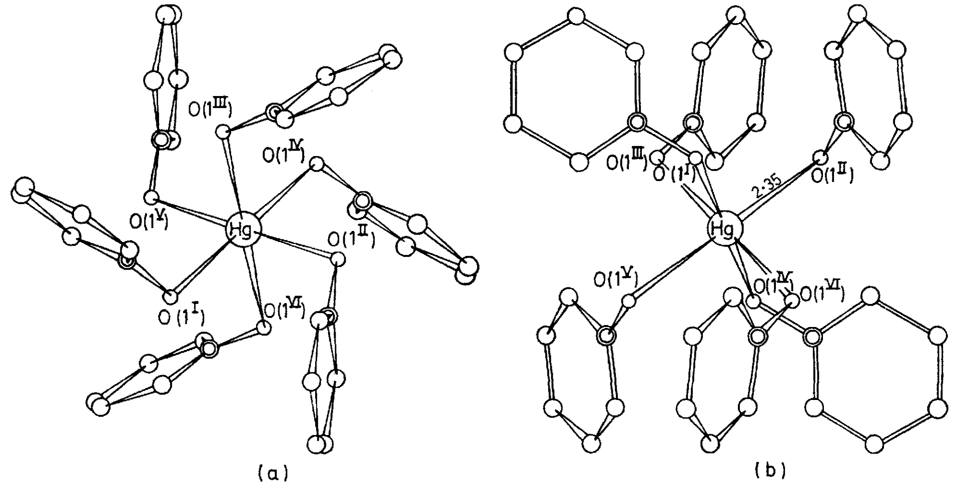

FIGURE 2 Projection of the [Hg(C$_5$H$_5$NO)$_6$]$^{2+}$ cation, (a) down the three-fold axis and (b) normal to the three-fold axis, showing the octahedral co-ordination

The mercury atom is co-ordinated by six pyridine 1-oxide ligands bonded *via* the oxygen atom, the oxygen atoms forming a regular octahedron. The mercury–oxygen distance [2·35(2) Å] is considerably larger than found in the digonally co-ordinated mercury(II) oxide (2·03 Å) [18,19] owing to the increase in co-ordination number, and is comparable to that found in the distorted tetrahedral co-ordination of HgCl$_2$(Ph$_3$AsO)$_2$, (2·35 Å).[20] In complexes of mercury(II) chloride with 3,5-dibromopyridine 1-oxide [21] and quinoline 1-oxide [22] longer distances of 2·51, and of 2·56 and 2·61 Å respectively were observed, the digonal Cl–Hg–Cl system remaining undistorted.

The octahedron of oxygen atoms is regular. Distortion of an octahedron having a three-fold rotation axis can be described in terms of the twist angle of the two trigonal faces relative to each other and a compression or elongation along the trigonal axis.[23] In the projection of the oxygen octahedron, the angle at the centre of the trigonal face between O(1$^{\mathrm{I}}$) and O(1$^{\mathrm{V}}$) is required by the $\bar{3}$ symmetry to be the ideal 60°. For a regular octahedron resting on a trigonal face of side a and of height h, the ratio $r = a/h = 1{\cdot}22$,[23] compared to a value of 1·21 ± 0·02 calculated for the oxygen octahedron. This lack of trigonal compression or elongation is reflected in the near equality of the two independent oxygen–oxygen distances [O(1$^{\mathrm{I}}$) · · · O(1$^{\mathrm{II}}$) 3·30(2), and O(1$^{\mathrm{I}}$) · · · O(1$^{\mathrm{V}}$), 3·34(2) Å]. This is the first structural evidence for the existence of a regular octahedral co-ordination of mercury.

The geometry of the co-ordinated pyridine 1-oxide molecule is in general agreement with the structure of the parent ligand; [24] in particular, the N–O bond length does not alter significantly on co-ordination [1·32(2), *cf.* ligand 1·35 Å]. The Hg–O–N angle [114(1)°] is intermediate between that required for sp^3 (109°) and sp^2 (120°) hybridisation of the oxygen atom. The dihedral angle between the pyridine ring plane and the Hg–O–N plane is 73°; similar observations have been made for other complexes [25] and it appears to result from the minimisation of non-bonded intermolecular repulsions.

There is no evidence for disordering or excessive thermal motion of the perchlorate oxygen atoms despite the lack of contacts <3·5 Å with the mercury atom. The closest intermolecular approach of perchlorate oxygen atoms is along the trigonal axis [2·97(9) Å], in excess of the van der Waal's contact (2·8 Å). The mean ion dimensions are Cl–O 1·39 Å, and O–Cl–O 109°. The site-symmetry of the perchlorate ion is C_{3v}; with this reduction of symmetry from the ideal T_d, it is expected that the degenerate i.r. (ν_3, ν_4) at *ca.* 1100 and 625 cm^{-1}

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will each split into two and the Raman band (ν_1) at *ca.* 930 cm^{-1} will become i.r.-active.[26] The i.r. spectrum of $[Hg(C_5H_5NO)_6](ClO_4)_2$ has bands at 938 (ν_1), 1127 and 1077 (ν_3), and 629 and 621 cm^{-1} (ν_4) assigned as vibrations of the perchlorate ion, these being the only bands not present in the spectrum of the free ligand. The splitting of ν_3 and ν_4 are consistent with the C_{3v} symmetry of the perchlorate ion derived from the structural study. Other investigations [7,27] have interpreted the i.r. spectrum of $[Hg(C_5H_5NO)_6](ClO_4)_2$ as showing no splitting of the perchlorate vibrational bands, consistent with there being no interaction of the anion with the mercury atom. While this conclusion is justified from the structural evidence, it is clear that a reduction from ideal symmetry of the perchlorate ion will lift the vibrational degeneracy of ν_3 and ν_4 and may result in splitting of these i.r. bands. Other workers [7] have assigned a band at 1213 cm^{-1} as the nitrogen–oxygen stretching frequency in the complex; no band was found at that frequency but a strong band assigned as ν(N–O) was observed at 1240 cm^{-1}. It was also reported from *X*-ray powder data that the unit cell of $[Hg(C_5H_5NO)_6](ClO_4)_2$ was tetragonal. Calculation of *d* spacings from the postulated cell and comparison with those found in the present structure shows a close similarity for the ten strongest reflections.

[2/2192 *Received*, 19*th September*, 1972]

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