Crystal Structure of the Dimeric Pyridine 1-Oxide Complex with Mercury(I) Perchlorate

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The crystal structure of the title compound, $[Hg(C_5H_5NO)_2(ClO_4)]_2$ has been determined by single-crystal *X*-ray diffraction by conventional heavy-atom methods. The structure was refined by a block-diagonal least-squares procedure to *R* 0·10 for 1502 independent visually estimated reflections. Crystals are triclinic, space group $P\bar{1}$, a = 8·68 ± 0·01, b = 12·76 ± 0·02, c = 14·00 ± 0·02 Å, α = 115·2 ± 0·1, β = 85·8 ± 0·1, γ = 97·5 ± 0·1°, Z = 2 dimers. The mercury(I) species is dimeric (Hg–Hg 2·523 ± 0·002 Å). The mercury co-ordination does not exhibit the usual two axially co-ordinated ligands; three of the four pyridine 1-oxide molecules bridge adjacent dimers, (Hg–O 2·19—2·77 Å) giving a mercury co-ordination number of 4 or 5. The perchlorate ions are subject to very high thermal motion and are ill-defined. Distances and angles within the pyridine 1-oxide molecules are as expected; the molecular plane does not contain the mercury atom. An improved preparative method for the complex is given.

THE few co-ordination compounds of mercury(I) whose structures have been reported invariably show the presence of the mercury dimer,[1-9] and, with the exception of the *o*-phenanthroline derivative,[9] are axially co-ordinated by the accompanying ligands; the usual stoicheiometry is (Hg_2X_2) or $(Hg_2L_2)X_2$. Preparative studies with a variety of oxygen donor ligands in the presence of the feebly co-ordinating perchlorate ion ($X = ClO_4^-$) have shown the existence of compounds of stoicheiometry $Hg_2L_4X_2$;[10] none of these have been structurally characterized.

In the expectation that unusual co-ordination of the mercury(I) dimer might be found in such complexes, we have undertaken a structural study of the pyridine 1-oxide derivative, $[Hg(C_5H_5NO)_2(ClO_4)]_2$.

EXPERIMENTAL AND RESULTS

Preparation.—A solution of mercury(I) perchlorate tetrahydrate (3·0 g, 4·5 mmol) in absolute methanol (10 ml) and triethyl orthoformate (5 ml) was added to a solution of freshly sublimed pyridine 1-oxide (4·0 g, 42 mmol) in the same mixed solvent (15 ml). The resulting immediate white precipitate was dissolved by the addition of absolute methanol (40 ml) and heating on a steam bath. The filtered solution was cooled in the dark, giving the complex as white needles which were washed successively with ice-cooled absolute methanol (2 ml) and ether (20 ml), dried in a vacuum desiccator overnight, and stored in a darkened container [2·4 g, m.p. 143 °C; Found: C, 24·65; H, 2·0; Cl, 7·1; Hg, 40·8; N, 5·50; O(difference), 19·95%. Calc. for $C_{10}H_{10}ClHgN_2O_6$: C, 24·5; H, 2·05; Cl, 7·25; Hg, 40·9; N, 5·7; O, 19·6%].

The apparent improvement over previous methods in this preparative technique is probably due to the presence of triethyl orthoformate and its dehydrating action[11] which inhibits the hydrolysis of the substance and prevents the formation of hydroxy- and oxide-compounds.

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Crystallography

Crystals were needles elongated along a. A single needle section closely approximating to a prism (0·10 × 0·12 × 0·12 mm) was used.

Non-integrated X-ray data were collected by the multiple-film equi-inclination Weissenberg method, with the crystal section mounted about a and b respectively for the layers 0—3kl, h0—2l; unit-cell calibration was effected by superimposing aluminium powder lines ($a_{298\,\mathrm{K}}$ 4·0494 Å)[12] on zero-layer photographs about all three axes. Nickel-filtered copper radiation was used throughout [$\lambda(K_{\alpha 1})$ 1·5406, $\lambda_{(\alpha 2)}$ 1·5444 Å].[13]

Crystal Data.—$C_{20}H_{20}Cl_2Hg_2N_4O_{12}$, M = 980·4, Triclinic, a = 8·68 ± 0·01, b = 12·76 ± 0·02, c = 14·00 ± 0·02 Å, α = 115·2 ± 0·1, β = 85·8 ± 0·1, γ = 97·5 ± 0·1°, U = 1390 Å^3, D_m = 2·35 ± 0·02 (flotation), Z = 2 dimers, D_c = 2·34, $F(000)$ = 916. Space group $P\bar{1}$ (No. 2, C_i^1).[14] μ(Cu-K_α) = 234 cm^{-1}; transmission coefficient range 0·092—0·236.

The intensities of 1502 independent observed reflections were estimated visually; only these non-zero reflections were included in the structure determination. The raw data were corrected for absorption,[15] and Lorentz and polarization factors and then scaled by internal correlation,[16] all reflections being assigned unit weights. Independent scale factors were used for sets of reflections from the upper and lower halves of the non-zero-layer photographs to offset the effects of spot-shape distortion.

Structure Determination.—The assumption of a dimeric mercury(I) species was vindicated by a three-dimensional unsharpened Patterson function computed on all data; the structure was solved in terms of two independent mercury atoms in space group $P\bar{1}$. The assumption that this symmetry described the disposition of the lighter atoms also was justified by the subsequent success of the structure determination. A structure-factor calculation on the basis of the mercury atoms alone with arbitrary isotropic thermal parameters B 3·0 Å^2 gave R 0·35. The chlorine atoms were located in a subsequent three-dimensional Fourier synthesis. Anisotropic thermal motion was quite pronounced, to the extent that no co-ordinated atoms could be distinguished confidently; refinement of positional and anisotropic thermal parameters of the form $\exp[-(h^2\beta_{11} + hk\beta_{12} + hl\beta_{13} + k^2\beta_{22} + kl\beta_{23} + l^2\beta_{33})]$ of the mercury atoms and of the chlorine, with isotropic thermal parameters, was carried out by a block-diagonal (3 × 3, 6 × 6) least-squares routine [local programs SFLS1,2 (by A. I. M. Rae)] the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. After three cycles R was 0·23 and subsequent Fourier syntheses located all remaining non-hydrogen atoms, although the oxygen atoms O(2i) bonded to Cl(2) were located only with much difficulty. With isotropic thermal parameters applied to all atoms except the mercury, atomic positional and thermal parameters refined to R 0·118. At this stage it was evident from the thermal parameters that both perchlorate ions were undergoing high thermal motion; a difference-Fourier synthesis phased by all other atoms gave no evidence for disorder of the oxygen sites. Accordingly all perchlorate oxygen atoms were refined with anisotropic thermal parameters; a weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced,[17] the constants a and b being redetermined as refinement proceeded to a final R of 0·104, and R' 0·144 {$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}. All parameter shifts finally were $<0{\cdot}2\sigma$ for the light atoms except those of the perchlorate oxygen atoms which were of the order of σ. A final difference-Fourier showed no unusual features, the largest peaks being of the order of $<0{\cdot}5$ of a carbon atom near the mercury sites. Final weighting scheme constants were a = 4·18, b = 0·0598.

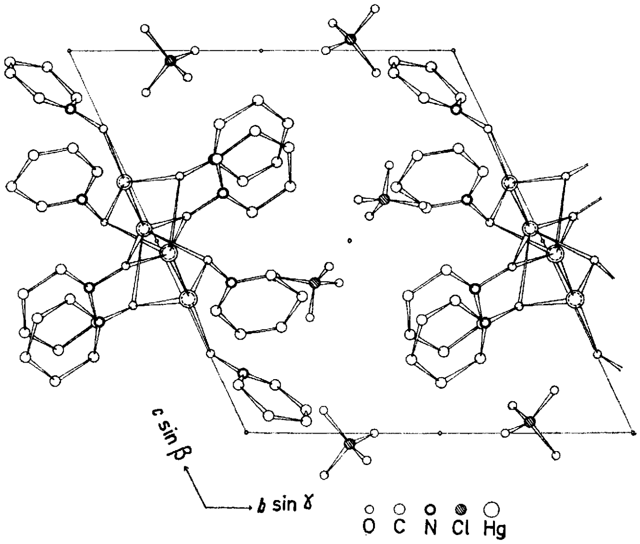

FIGURE 1 The unit cell contents viewed in projection on (a) [100] and (b) [010]

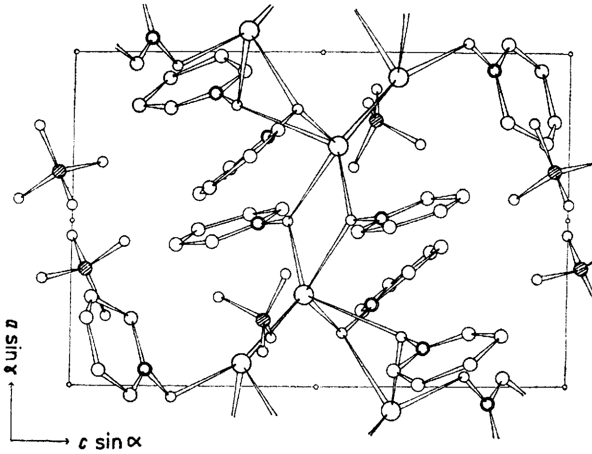

FIGURE 2 The asymmetric unit, showing the atomic numbering system used

Scattering factors employed for neutral chlorine, oxygen, nitrogen, and carbon atoms, and for singly charged mercury were taken from refs. 18 and 19, that for mercury being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[20] The final

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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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[16] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[17] D. W. Cruickshank in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 114.

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[19] D. T. Cromer, *Acta Cryst.*, 1965, **19**, 224.

[20] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

set of observed and calculated structure factors are given in Supplementary Publication No. SUP 20575 (4 pp., 1 microfiche).* Final atomic fractional cell and thermal parameters are given in Table 1, with least-squares estimated standard deviations, which should be treated circumspectly in view of the block-diagonal refinement procedure. The unit-cell contents are depicted in Figures 1 and 2; Figure 3 gives the asymmetric unit and atom numbering system. Interatomic distances and angles are given in Table 2 and least-squares planes of the ligands in Table 3.

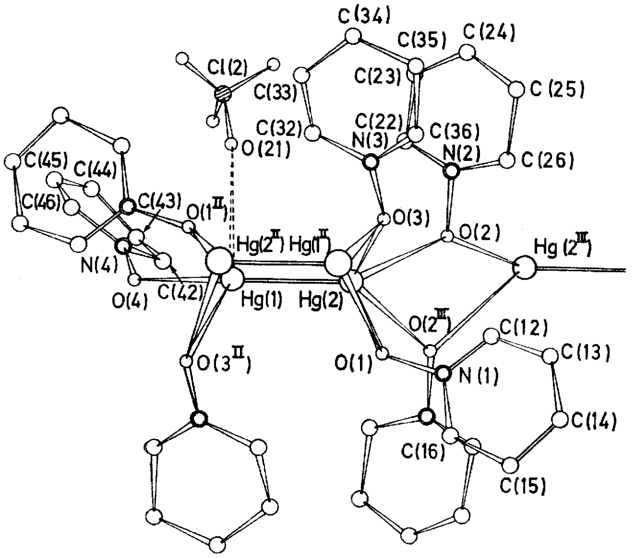

FIGURE 3

Computation was carried out on a DEC PDP 10 at the University of Western Australia.

TABLE 1

Atomic positional co-ordinates and thermal parameters (Å^2), with standard deviations in parentheses

Atom	x	y	z	B
Hg(1)	0·0717(2)	0·0136(2)	0·3478(1)	*
Hg(2)	0·2756(2)	0·0175(2)	0·4690(1)	*
Cl(1)	0·355(2)	0·747(1)	0·029(1)	8·3(3)
O(11)	0·212(4)	0·721(5)	0·072(4)	*
O(12)	0·325(6)	0·773(5)	−0·059(4)	*
O(13)	0·436(4)	0·848(3)	0·110(3)	*
O(14)	0·454(5)	0·670(3)	−0·001(3)	*
Cl(2)	0·202(1)	0·359(1)	0·390(1)	7·8(3)
O(21)	0·148(7)	0·266(4)	0·407(5)	*
O(22)	0·340(7)	0·417(9)	0·434(5)	*
O(23)	0·107(8)	0·423(8)	0·392(11)	*
O(24)	0·272(13)	0·305(9)	0·302(8)	*
O(1)	0·164(3)	−0·112(2)	0·549(2)	5·8(5)
N(1)	0·248(3)	−0·145(2)	0·608(2)	4·4(5)
C(12)	0·344(5)	−0·071(3)	0·681(3)	6·2(9)
C(13)	0·419(6)	−0·104(4)	0·744(3)	8·2(11)
C(14)	0·402(5)	−0·219(3)	0·724(3)	6·3(9)
C(15)	0·307(6)	−0·312(4)	0·642(3)	8·6(12)
C(16)	0·228(5)	−0·259(3)	0·588(3)	6·6(9)
O(2)	0·502(3)	0·109(2)	0·564(2)	7·2(6)
N(2)	0·507(4)	0·231(2)	0·624(2)	6·2(7)
C(22)	0·465(5)	0·284(4)	0·576(3)	7·1(10)
C(23)	0·482(6)	0·413(4)	0·641(4)	9·1(12)
C(24)	0·528(6)	0·457(4)	0·744(4)	9·6(13)
C(25)	0·574(8)	0·391(6)	0·789(5)	13·6(20)
C(26)	0·566(5)	0·257(4)	0·716(3)	7·2(10)
O(3)	0·154(3)	0·140(2)	0·670(2)	5·4(5)
N(3)	0·116(4)	0·247(3)	0·713(2)	6·8(7)
C(32)	0·050(5)	0·296(4)	0·655(3)	7·2(10)
C(33)	0·007(7)	0·407(5)	0·705(4)	10·6(15)
C(34)	0·071(10)	0·484(7)	0·809(6)	17·4(27)
C(35)	0·153(8)	0·435(6)	0·869(5)	12·9(19)
C(36)	0·161(6)	0·305(4)	0·805(4)	8·6(11)
O(4)	−0·034(3)	0·004(2)	0·206(2)	5·9(5)
N(4)	0·051(4)	0·064(3)	0·154(2)	6·8(7)
C(42)	0·206(5)	0·037(4)	0·124(3)	7·2(10)
C(43)	0·270(7)	0·077(5)	0·044(4)	11·0(15)
C(44)	0·207(7)	0·168(5)	0·031(4)	11·4(17)
C(45)	0·049(5)	0·181(4)	0·059(3)	7·6(10)
C(46)	−0·029(4)	0·133(3)	0·124(2)	6·2(8)

* Anisotropic thermal parameters ($\times 10^3$).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	17·7(3)	13·2(1)	10·5(1)	3·0(5)	−7·1(3)	12·5(3)
Hg(2)	17·3(3)	15·4(1)	11·2(1)	1·8(5)	−8·3(3)	15·3(3)
O(11)	25(7)	53(10)	28(5)	−2(17)	12(10)	56(13)
O(12)	55(13)	57(10)	26(5)	49(20)	16(13)	63(13)
O(13)	35(8)	27(5)	17(3)	2(12)	−10(8)	21(7)
O(14)	52(11)	25(5)	16(3)	50(14)	17(10)	10(7)
O(21)	65(17)	29(6)	47(8)	−32(16)	−35(19)	63(12)
O(22)	44(12)	100(25)	34(9)	−75(36)	−31(17)	42(23)
O(23)	41(14)	65(16)	144(33)	3(23)	−56(34)	167(42)
O(24)	140(46)	58(18)	41(12)	33(43)	−81(44)	4(24)

DISCUSSION

As is usual in mercury(I) complexes, the mercury exists as a dimeric species, Hg_2, the dimers lying approximately in the (010) plane. The Hg–Hg distance of 2·523 ± 0·002 Å agrees well with previous distances found for this species which, in more accurate determinations, vary between 2·50 and 2·52 Å.[21] Adjacent dimers are separated by Hg ··· Hg distances of 3·90 [Hg(1) ··· Hg(2^{II})] and 4·17 Å [Hg(2) ··· Hg(2^{III})], the atoms in the latter case being centrosymmetrically related. Each of these distances is rather larger than the estimated van der Waal's contact of 3·0 Å,[22] and arises out of the bridging action of the pyridine 1-oxide molecules. The Hg(1) ··· Hg(2^{II}) distance is spanned by the oxygen atoms O(1^{II}) and O(3^{II}) [Hg(1) ··· O(1^{II}) 2·55, Hg(1) ··· O(3^{II}) 2·53, Hg(2^{II}) ··· O(1^{II}) 2·43 and Hg(2^{II}) ··· O(3^{II}) 2·77 Å]; the Hg(2) ··· Hg(2^{III}) distance is spanned by O(2) and O(2^{III}) arising out of the associated centrosymmetric pair of ligands (2) [Hg(2) ··· O(2) 2·34, Hg(2) ··· O(2^{III}) 2·56 Å].

The environment of each mercury atom may be described in terms of mercury–oxygen contacts of less than the van der Waal's estimate of 2·9 Å[22,23] as follows: the ' co-ordination ' of Hg(1) consists of a very irregular tetrahedron composed of Hg(2), the bridging oxygen atoms at 2·53 and 2·55 Å, and a further close Hg ··· O contact to ligand (4) [Hg(1) ··· O(4) 2·19 Å]. The angles are very irregular ranging from 70 [O(1^{II}) ··· Hg(1) ··· O(3^{II})] to 160° [Hg(2)—Hg(1) ··· O(4)]. The ' co-ordination ' of Hg(2) is an irregular five-co-ordination imposed by Hg(1) and the bridging oxygen atoms to Hg(2^{III}) and to Hg(1^{II}) at distances 2·34, 2·43, 2·56, and 2·77 Å. The angles range from 63 [O(2) ··· Hg(2) ···

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[21] Ref. 7, see Table 5.

[22] D. Grdenić, *Quart. Rev.*, 1965, **19**, 303.

[23] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., University Press, Ithaca, New York, 1960, p. 260.

TABLE 2

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

(*a*) Bonding distances and angles within the discrete Hg_2, ClO_4, and C_5H_5NO entities *

(i) Distances

Perchlorate (1)		Perchlorate (2)	
⟨Cl(1)–O(1*i*)⟩	1·40(5)	⟨Cl(2)–O(2*i*)⟩	1·30(8)
Ligand (1)		Ligand (2)	
O(1)–N(1)	1·37(4)	O(2)–N(2)	1·42(4)
⟨N(1)–C(12,16)⟩	1·33(5)	⟨N(2)–C(22,26)⟩	1·36(5)
⟨C–C⟩	1·42(6)	⟨C–C⟩	1·45(8)
Ligand (3)		Ligand (4)	
O(3)–N(3)	1·32(4)	O(4)–N(4)	1·38(4)
⟨N(3)–C(32,36)⟩	1·32(6)	⟨N(4)–C(42,46)⟩	1·41(6)
⟨C–C⟩	1·46(9)	⟨C–C⟩	1·43(8)

(ii) Angles

Perchlorate (1)		Perchlorate (2)	
⟨O(1*i*)–Cl(1)–O(1*j*)⟩	109(3)	⟨O(2*i*)–Cl(2)–O(2*j*)⟩	109(6)
Ligand (1)		Ligand (2)	
⟨O(1)–N(1)–C(12,16)⟩	119(3)	⟨O(2)–N(2)–C(22,26)⟩	111(3)
⟨N(1)–C–C⟩	122(4)	⟨N(2)–C–C⟩	112(4)
⟨C–C–C⟩	117(4)	⟨C–C–C⟩	119(6)
Ligand (3)		Ligand (4)	
⟨O(3)–N(3)–C(32,36)⟩	118(4)	⟨O(4)–N(4)–C(42,46)⟩	117(3)
⟨N(3)–C–C⟩	122(4)	⟨N(4)–C–C⟩	115(4)
⟨C–C–C⟩	117(6)	⟨C–C–C⟩	119(5)

(*b*) Selected distances (Å) <3·5 Å between the Hg_2 and ClO_4 and C_5H_5NO species and associated angles.

(i) Contacts about the mercury atoms

Hg(1) ··· O(1^{II})	2·55(2)	Hg(2) ··· O(1)	2·43(3)
Hg(1) ··· O(3^{II})	2·53(3)	Hg(2) ··· O(2)	2·34(3)
Hg(1) ··· O(4)	2·19(2)	Hg(2) ··· O(2^{III})	2·56(3)
Hg(1) ··· O(21)	2·96(6)	Hg(2) ··· O(3)	2·77(2)

(ii) The angular environment of the mercury atoms (°)

Hg(2)–Hg(1) ··· O(1^{II})	111·7(6)
Hg(2)–Hg(1) ··· O(3^{II})	111·8(6)
Hg(2)–Hg(1) ··· O(4)	159·9(7)
Hg(2)–Hg(1) ··· O(21)	91·0(10)
Hg(1) ··· O(1^{II})–N(1^{II})	112(2)
Hg(1) ··· O(3^{II})–N(3^{II})	114(2)
Hg(1) ··· O(4)–N(4)	116(2)
Hg(1) ··· O(21)–Cl(2)	156(4)
Hg(1)–Hg(2) ··· O(1)	105·9(6)
Hg(1)–Hg(2) ··· O(2)	149·2(7)
Hg(1)–Hg(2) ··· O(2^{III})	131·2(6)
Hg(1)–Hg(2) ··· O(3)	103·8(6)
Hg(2) ··· O(1)–N(1)	123(2)
Hg(2) ··· O(2)–N(2)	115(2)
Hg(2) ··· O(2^{III})–N(2^{III})	128(2)
Hg(2) ··· O(3)–N(3)	129(2)

Roman numerals as superscripts denote the following equivalent positions:

II $\bar{x}, \bar{y}, 1 - z$ III $1 - x, \bar{y}, 1 - z$

* Hg–Hg is 2·523(2); because of the large inaccuracy in the remainder of the dimensions and angles, many of which are well known already and similar, only the mean distances, angles and σ values are given within each individual perchlorate and ligand entity. In no case is the deviation of any individual value from the mean >2σ.

O(2^{III})] to 149° [Hg(1)—Hg(2) ··· O(2)]. There is a very long perchlorate contact to Hg(1) [Hg(1) ··· O(21) 2·96 Å].

In previously studied complexes of mercury(I) with oxygen donor ligands, all investigations show a short axial co-ordination [Hg ··· O 2·08—2·24 Å],[2,6] with long contacts in the perpendicular plane; in this complex, the many mercury–oxygen distances are appreciably and variably longer on the whole, as a consequence of the multiple and irregular array of ligating and bridging oxygen atoms. A crude correlation exists between the size of the Hg–Hg ··· O angle and the Hg ··· O distance, the latter decreasing as the former approaches 180°, and, in the case of the angle Hg(2)–Hg(1) ··· O(4) (160°), the corresponding distance is 2·19 Å which is comparable with the values found in systems with axial co-ordination.[2-6,8,9] This distance is confirmatory evidence for the strong axial acceptor properties of the mercury(I) ion.[7] It is also very much shorter than the mercury(II)–oxygen distances (2·56, 2·61, and 2·51 Å) found in the complexes of mercury(II) chloride formed with quinoline 1-oxide[24] and 3,5-dibromopyridine 1-oxide;[25] the mercury co-ordination in these latter complexes is irregular 'octahedral' and 'trigonal,' some of the chlorine contacts in the co-ordination spheres being long.

TABLE 3

Equations * of least-squares planes through the ligands, computed on all atoms, in the form $lX + mY + nZ = p$; atomic deviations (Å) from the planes in square brackets

	l	m	n	p	σ
Ligand (1):	0·738	0·134	−0·662	3·593	0·02
[O(1) −0·02, N(1) 0·01, C(12) 0·04, C(13) −0·02, C(14) −0·02, C(15) 0·02, C(16) 0·00]					
Ligand (2):	0·902	0·270	−0·337	1·364	0·02
[O(2) 0·00, N(2) −0·02, C(22) −0·02, C(23) 0·04, C(24) −0·02, C(25) −0·01, C(26) 0·03]					
Ligand (3):	0·818	0·449	−0·359	−2·592	0·06
[O(3) 0·04, N(3) −0·04, C(32) 0·07, C(33) −0·08, C(34) 0·05, C(35) 0·04, C(36) 0·06]					
Ligand (4):	0·308	0·477	0·823	1·639	0·08
[O(4) −0·07, N(4) 0·07, C(42) 0·10, C(43) −0·15, C(44) 0·08, C(45) −0·04, C(46) 0·01]					

* The orthogonal (Å) frame (X,Y,Z) is derived from the triclinic cell by the transformation:

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

The geometry of the pyridine 1-oxide and perchlorate species is not well defined owing to the dominance of the scattering by the mercury atoms; in addition the situation is complicated by the very high thermal motion of the perchlorate groups, particularly group (2). The geometry of the pyridine 1-oxide ligands does not differ significantly from the values hitherto observed in the free molecule[26] and in other complexes[27-31] (⟨N–O⟩ 1·37 ± 0·02, ⟨C–N⟩ 1·33 ± 0·03, ⟨C–C⟩ 1·44 ± 0·03). The

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same is probably true of the perchlorate geometry [⟨Cl(1)–O⟩ 1·40 ± 0·03]; however, in perchlorate (2), ⟨Cl(1)–O⟩ is 1·30 ± 0·03, the discrepancy probably being due to the high thermal motion. The perchlorate groups display no close contacts with adjacent atoms [Table 2(b)], with the possible exception of Hg(1) · · · O(21) (2·96 Å). All pyridine 1-oxide species may be considered as ' bound ' to a neighbouring mercury atom, albeit in an irregular manner, at distances significantly shorter than the van der Waal's distance. The Hg · · · O–N angles range from 112—129°.

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