Crystal Structure of Bis[(3-chloropyridine)mercury(I)] Diperchlorate

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The crystal structure of the title compound, has been determined by single-crystal *X*-ray diffraction methods. The structure was solved by conventional heavy atom methods, and refined by block-diagonal least squares to *R* 0·114 for 625 independent visually observed reflections. Crystals are monoclinic, space group *C*2/*m*, *a* = 16·49 ± 0·02, *b* = 22·92 ± 0·04, *c* = 5·04 ± 0·01 Å, β = 92·4 ± 0·1°. There are four dimers per unit cell, the asymmetric unit being half a dimer. Hg–Hg is 2·487 Å, and is approximately axially co-ordinated by the ligand (Hg–N 2·21 Å, Hg–Hg–N 167·4°). There are two independent perchlorate ions in the cell.

We have previously determined the crystal structure of $[Hg_2(4\text{-cyanopyridine})_2]^{2+}$ $[ClO_4^-]_2$, the first reported example of the mercury dimer axially co-ordinated by a pair of nitrogen donor ligands.[1] In this complex, the possibility existed that the observed planarity of the cation was a consequence of electron delocalization from the conjugated ligands through the mercury dimer. To test this observation we have extended the investigation of the structures of complexes formulated as $Hg_2L_2(ClO_4)_2$ (where L is a nitrogen base), and now report the crystal structure of the analogous complex with 3-chloropyridine. The preparation is also described.

EXPERIMENTAL

Preparation.—3-Chloropyridine (2·02 g) was diluted with anhydrous methanol (10 ml) and filtered. A solution of mercury(I) perchlorate (3·0 g) in $(EtO)_3CH$ (5·0 ml) was filtered into the ligand solution,[2] and set aside overnight when a small crystalline precipitate was obtained. Further deposits were obtained when the solution was set aside for some time. Addition of anhydrous ether (20 ml) to the filtrate gave a further immediate white precipitate of the substance, m.p. 260—1 °C [Found: C, 14·65; H, 1·05; Cl, 17·0; Hg, 48·5; N, 3·25; O (difference), 15·7. $C_{10}H_8Cl_4Hg_2N_2O_8$ requires C, 14·50; H, 1·0; Cl, 17·15; Hg, 48·5; N, 3·4; O, 15·5%].

Crystals were needles, elongated along *c*. A single needle section in the form of a triangular prism [0·13 (base, *a*) × 0·076 (height, *b*) × 0·20 (length, *c*) mm] was used for the crystal structure analysis.

Non-integrated *X*-ray data were collected by use of the multiple-film equi-inclination Weissenberg method, the crystal being mounted about *c* and *b* respectively for the layers *hk*0—2, *h*0—1*l*; unit-cell calibration was effected by superimposing aluminium powder lines (a_{298K} = 4·0494 Å)[3] on zero-layer photographs about *b* and *c*. Nickel-filtered copper radiation was used throughout [$\lambda(K_\alpha)$ = 1·5418 Å].[4]

Crystal Data.—$C_5H_4Cl_2HgNO_4$, *M* = 413·6, Monoclinic, *a* = 16·49 ± 0·02, *b* = 22·92 ± 0·04, *c* = 5·04 ± 0·01 Å, β = 92·4 ± 0·1°, *U* = 1904 Å^3, D_m = 2·81 ± 0·05 (by flotation), *Z* = 8, D_c = 2·89, *F*(000) = 1496. Space group *C*2/*m* (No. 12, C^3_{2h}) [5] from systematic absences: $h + k = 2n + 1$. μ(Cu-K_α = 363 cm^{-1}); μ*r* 0·041—0·267.

There was no evidence of decomposition during exposure to *X*-rays.

The intensities of 638 independent observed reflections were estimated visually by use of a calibrated strip and used in the structure determination. The raw data were corrected for absorption,[6] Lorentz, and polarization factors and scaled by internal correlation,[7] all reflections being assigned unit weights.

Structure Determination.—A three-dimensional sharpened Patterson function was computed on all data. Systematic absences were consistent with three possible space groups: *C*2/*m*, *C*2, and *Cm*. The Patterson function was dominated by mercury vectors (0,2*y*,0), (2*x*,0,2*z*), and (2*x*,2*y*,2*z*), the last indicating that for the mercury atoms at least, the correct space group was *C*2/*m* (confirmed by the subsequent successful refinement). The Patterson function was solved

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[1] D. L. Kepert, D. Taylor, and A. H. White, *Inorg. Chem.*, 1972, **11**, 1639.

[2] D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, 1973, 392.

[3] B. W. Delf, *J. Appl. Phys.*, 1963, **14**, 345.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 9162, p. 59.

[5] Ref. 4, vol. I, 1965, p. 95.

[6] N. W. Alcock, in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271, program ABSCOR.

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

for one independent mercury atom per unit cell; the usual Hg_2 dimeric species was generated by the application of a C_2 operation. A structure-factor calculation on the basis of the mercury atom alone with an arbitrary isotropic thermal parameter B 3·0 Å^2 gave R 0·32. The chlorine atoms were located from a three-dimensional Fourier synthesis; two independent sets were located at a series of special positions generated from $(0,y,\frac{1}{2})$ and $(x,0,z)$, corresponding to the perchlorate ions, a third chlorine belonging to the ligand being found in a general position. With arbitrary isotropic thermal parameters of 5·0 Å^2 for these atoms, R was further reduced to 0·22. All non-hydrogen light atoms were located from a difference Fourier. The structure was refined with several cycles of block-diagonal least-squares (3 × 3, 6 × 6) to R 0·176, with local versions of the programs SFLS 1 and 2 by A.I.M. Rae. With anisotropic thermal parameters in the form $\exp[-\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$ introduced for the mercury and ligand chlorine atoms, R was reduced to 0·141. A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced,[8] a and b being adjusted as refinement proceeded to minimize the function $\Sigma w(|F_o| - |F_c|)^2$; R was reduced to 0·128. A structure-factor calculation at this stage showed **13** reflections with $\sin^2\theta/\lambda^2 < 0·04$ to be apparently heavily affected by extinction. These were rejected if $(|F_c| - |F_o|) > 70$. (In the final Table of $|F_o|$ and $|F_c|$ these are included and underlined). A further refinement converged at R 0·114 and R' 0·147 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. The final value for a was 3·35, and b 0·075.

Table 1

(*a*) Final atomic fractional cell parameters and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Hg	0·07527(8)	0·11226(6)	−0·0074(4)	*
Cl(3)	0·4126(7)	0·078(1)	0·258(6)	*
N(1)	0·206(1)	0·133(1)	−0·032(6)	4·7(6)
C(2)	0·254(2)	0·107(1)	0·091(9)	5·3(9)
C(3)	0·342(3)	0·119(2)	0·073(13)	7·9(11)
C(4)	0·366(2)	0·157(1)	−0·083(8)	5·8(8)
C(5)	0·310(4)	0·187(3)	−0·183(13)	12·2(17)
C(6)	0·228(3)	0·176(2)	−0·178(12)	9·1(12)
Cl(1)	0·000(†)	0·2300(7)	0·500(†)	7·1(3)
O(11)	0·069(2)	0·202(2)	0·439(8)	12·3(12)
O(12)	0·021(4)	0·263(3)	0·698(15)	19·8(20)
Cl(2)	0·1493(7)	0·000(†)	0·601(3)	4·8(2)
O(21)	0·119(1)	0·050(1)	0·485(6)	7·5(6)
O(22)	0·235(2)	0·000(†)	0·576(11)	8·8(10)
O(23)	0·128(2)	0·000(†)	0·891(1)	8·2(10)

* Anisotropic thermal parameters (×10^4) † Special coordinate.

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Hg	34·3(8)	−4·4(6)	33(5)	29·8(4)	−12·4(3)	639(7)
Cl(3)	51(6)	15(11)	95(67)	91(8)	654(89)	3023(313)

(*b*) Thermal ellipsoids of the mercury atom and Cl(3). Root-mean-square vibrational amplitudes U_{ii} (Å × 10^3) along the principal axes are given; their direction cosines (l, m, n all ×10^3) are expressed relative to an orthogonal (Å) frame where $X = ax + cz \cos\beta$, $Y = by$, and $Z = cz \sin\beta$. The angle θ between the principal axis and Hg–Hg bond is given, together with the angle ϕ between the principal axis and the normal to the ligand plane

Atom	U_{ii}	l	m	n	θ	ϕ
Hg	215	990	112	−87	9·3	86·6
	277	−40	811	584	88·7	15·0
	292	136	−575	807	80·8	75·4
Cl(3)	242	897	−334	291		87·5
	351	439	756	−486		85·8
	722	−58	536	824		4·9

In the final cycle of least squares all parameter shifts were <0·25σ for the light atoms and <0·06σ for mercury. A final difference-Fourier synthesis was substantially flat, the largest peak being of the order of 0·5 carbon at the mercury site. Although perchlorate thermal parameters were high, they were stable during refinement and there is no evidence for positional disorder.

Scattering factors employed were for monovalent mercury, [corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$)], otherwise for neutral atoms.[9–11] Final observed and calculated structure factors are listed in Supplementary Publication. No. SUP 20657 (3 pp., 1 microfiche).* Final atomic positional and thermal parameters are given in Table 1, together with least squares estimated standard deviations,

Table 2

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

(*a*) The cation

Hg–N(1)	2·21(2)	Hg$^{\mathrm{I}}$–Hg–N(1)	167·4(7)
N(1)–C(2)	1·16(5)	Hg–N(1)–C(2)	120(2)
C(2)–C(3)	1·48(7)	Hg–N(1)–C(6)	120(3)
C(3)–C(4)	1·25(6)	C(2)–N(1)–C(6)	120(4)
C(4)–C(5)	1·24(7)	N(1)–C(2)–C(3)	122(4)
C(5)–C(6)	1·38(8)	C(2)–C(3)–C(4)	120(5)
C(6)–N(1)	1·29(6)	C(3)–C(4)–C(5)	113(5)
C(3)–Cl(3)	1·73(6)	C(4)–C(5)–C(6)	128(6)
Hg–Hg$^{\mathrm{I}}$	2·487(2)	C(5)–C(6)–N(1)	116(5)
		Cl(3)–C(3)–C(2)	120(4)
		Cl(3)–C(3)–C(4)	120(4)

(*b*) The perchlorate anion

Cl(1)–O(11)	1·35(4)	O(11)–Cl(1)–O(12)	105(3)
Cl(1)–O(12)	1·28(7)	O(11)–Cl(1)–O(12$^{\mathrm{IX}}$)	108(3)
Cl(2)–O(21)	1·37(3)	O(12)–Cl(1)–O(12$^{\mathrm{IX}}$)	109(4)
Cl(2)–O(22)	1·43(4)	O(21)–Cl(2)–O(21)	113(2)
Cl(2)–O(23)	1·52(5)	O(21)–Cl(2)–O(22)	108(2)
		O(21)–Cl(2)–O(23)	108(2)
O(11)–Cl(1)–O(11$^{\mathrm{IX}}$)	122(3)	O(23)–Cl(2)–O(22)	111(2)

(*c*) Contacts <3·5 Å, and selected associated angles (deg.)

Hg · · · O(11)	3·05(4)	N · · · O(21$^{\mathrm{II}}$)	3·37(4)
Hg · · · O(21)	2·93(3)	N · · · O(23$^{\mathrm{II}}$)	3·33(3)
Hg · · · O(21$^{\mathrm{II}}$)	3·04(3)	C(2) · · · O(21)	3·21(5)
Hg · · · O(11$^{\mathrm{II}}$)	3·46(4)	C(2) · · · O(22)	3·49(5)
Hg · · · O(23$^{\mathrm{II}}$)	2·77(2)	C(2) · · · O(22$^{\mathrm{II}}$)	3·35(4)
		C(4) · · · O(12$^{\mathrm{III}}$)	3·22(7)
O(21) · · · Hg–Hg	100·7(5)	C(4) · · · O(12$^{\mathrm{IV}}$)	3·38(7)
O(23$^{\mathrm{II}}$) · · · Hg–Hg$^{\mathrm{I}}$	109·0(7)	C(6) · · · O(11$^{\mathrm{II}}$)	3·25(6)
		O(12) · · · O(12$^{\mathrm{V}}$)	3·15(10)

(*d*) Chlorine-chlorine contacts <4·0 Å

Cl(3) · · · Cl(3$^{\mathrm{VI}}$)	3·59(3)	Cl(3) · · · Cl(3$^{\mathrm{VIII}}$)	3·96(3)
Cl(3) · · · Cl(3$^{\mathrm{VII}}$)	3·70(3)		

Transformations of the asymmetric unit (x, y, z) are defined by Roman numeral superscripts:

I	$\bar{x}, y, \bar{z}$	VI	$x, \bar{y}, z$
II	$x, y, z - 1$	VII	$1 - x, y, 1 - z$
III	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$	VIII	$1 - x, y, \bar{z}$
IV	$\frac{1}{2} + x, \frac{1}{2} - y, z - 1$	IX	$\bar{x}, y, 1 - z$
V	$\bar{x}, y, 2 - z$		

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue. Items less than 10pp are sent as full size copies.

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

[9] D. T. Cromer and A. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

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

derived by a block-diagonal routine and therefore probably underestimated. Interatomic distances and angles [12] are listed in Table 2; a least-squares plane for the ligand is given in Table 3. Unit-cell contents are depicted in Figure 1, which gives the atomic numbering system used. Computing was carried out on a DEC PDP 10 at the University of Western Australia.

TABLE 3

Least-squares plane through the pyridine ring, referred to an orthogonal frame (X,Y,Z) defined in Table 1, with atomic deviations (Å); standard deviations of atoms defining the plane are 0·03 Å

Plane: N(1), C(2)—(6)

$$-0{\cdot}064X + 0{\cdot}631Y + 0{\cdot}773Z = 1{\cdot}613$$

N(1) −0·03, C(2) 0·02, C(3) 0·03, C(4) −0·06, C(5) 0·04, C(6) 0·00, Cl(3) 0·09, Hg −0·10

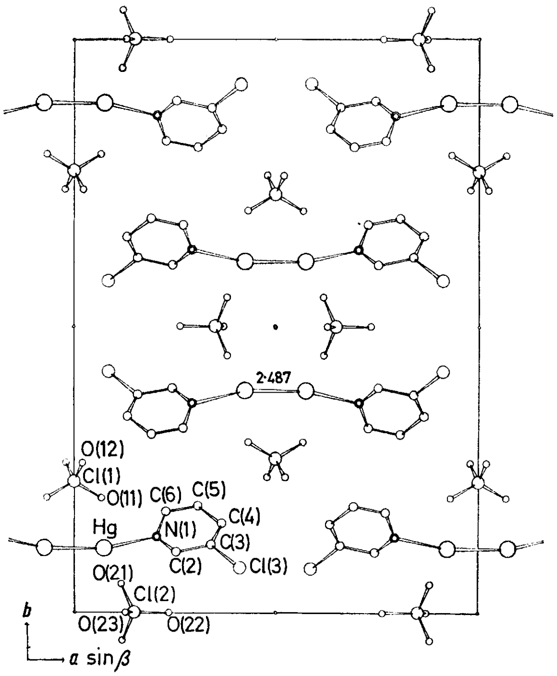

FIGURE 1 Projection of the unit cell contents on [001], together with atomic numbering systems

DISCUSSION

It is well known that the reaction of bases such as ammonia or pyridine with mercury(I) salts results in disproportionation to metallic mercury and the amine complex of mercury(II).[13,14] However, by use of a substituted pyridine base of lower basicity (4-cyanopyridine, pK_a 1·86, *cf.* pyridine pK_a 5·21),[15] a stable addition complex of mercury(I) perchlorate has been formed; the isolation and structural investigation of the mercury(I) perchlorate complex with 3-chloropyridine (pK_a 2·81) [15] confirms the formation of stable derivatives under these conditions.[1]

The crystal structure consists of dimeric $[Hg_2(C_5H_4NCl)_2]^{2+}$ cations and perchlorate anions. The mercury dimers lie approximately parallel to the (001) plane with the two-fold monoclinic *b* axis perpendicular to the mercury–mercury bond at its mid-point; only half of the cation is crystallographically independent. There are two distinct perchlorate ions in the lattice, the chlorine atoms being located either on a mirror plane or a two-fold axis. The nearest neighbouring Hg_2 species are those related by the $(x,0,z)$ mirror (5·15 Å) and the *c* unit translation (5·04 Å); these dimers are associated with the perchlorate ions centred on the mirror plane and pack to form columns parallel to *c*.

The $[Hg_2(C_5H_4NCl)_2]^{2+}$ cation consists of the mercury dimer co-ordinated by the basic nitrogen atom of the 3-chloropyridine molecules, giving effectively digonal co-ordination for each mercury atom {Hg–Hg 2·487, Hg–N, 2·21 Å; in $[Hg_2(C_6H_4N_2)_2]^{2+}$, Hg–Hg 2·498(2), Hg–N, 2·16(3) Å}. The Hg–Hg–N angle is 167°; in the $[Hg_2(C_6H_4N_2)_2]^{2+}$ cation,[1] the corresponding angle is 176°. This distortion of the ligand from perfect linear co-ordination is attributed in the present structure to repulsion between the chlorine substituents on the ligands of neighbouring cations related by the mirror plane, the distance [3·59(3) Å] being very close to the van der Waal's distance (3·6 Å).[16] Other similar distances of 3·70(3) and 3·96(3) Å are also observed. A further consequence of this steric strain may be the marked deviation from planarity of the cation, the dihedral angle between the two ligand planes being 78·3°, in

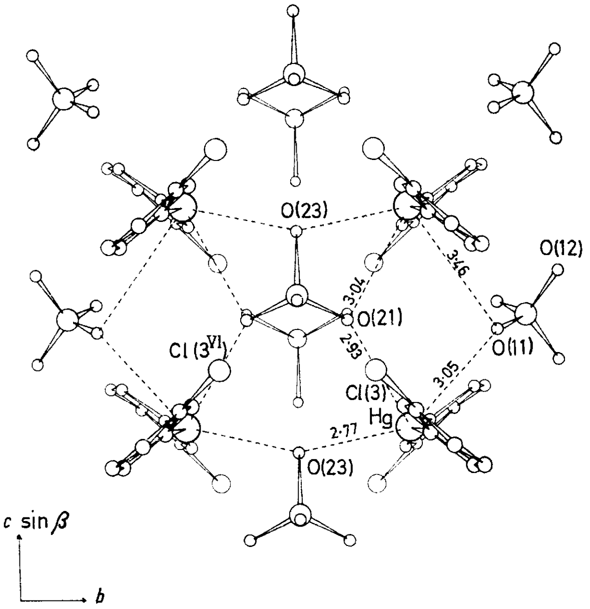

FIGURE 2 Projection of a columnar unit down [100] showing perchlorate contacts

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[13] W. Lang, *Ber.*, 1888, **21**, 1578.

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[15] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.

[16] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.

contrast to the centrosymmetric $[Hg_2(C_6H_4N_2)_2]^{2+}$ cation,[1] where the corresponding angle is 0°; although Hg–N is longer in the present structure, the significance of the difference is low and the discrepancy should not be attributed to the destruction of possible conjugation; if real, it is probably as much a consequence of the increased Hg–Hg–N angle. In addition, the thermal motion of the chlorine atom is grossly anisotropic, the longest principal axis of the ellipsoid being normal to the ligand plane. A further cause of cation distortion originates in the constraint on the mercury atoms in adjacent dimers by the significant and symmetrical bonding of the perchlorate oxygen [0(23), Figure 1]; this is the only other significant contact to the mercury which is less than the van der Waal's distance.[16,17] {A similar long Hg–O bond (2·77 Å) to one of the bridging pyridine 1-oxide ligands is found in the structure of $[Hg_2(C_5H_4NO)_4](ClO_4)_2$.[2]}

The precision of the ligand geometry is low, owing to the dominance of the *X*-ray scattering by the mercury atoms, and because of the high thermal motion of the molecule arising out of the large out-of-plane component of the chlorine substituent vibration. The pyridine ring is planar, with both chlorine and mercury atoms out of the plane by *ca.* 3σ.

The independent perchlorate ions have site-symmetry C_2 and C_s respectively. Oxygen atom O(11) spans the mercury atoms of the adjacent dimeric units related by the *c* unit translation at very long distances (Hg–O 3·05 and 3·46 Å) with consequent high thermal motion, resulting in shortened Cl–O distances [Cl(1)–O(11) 1·28 and Cl(1)–O(12) 1·35; ideal 1·45 Å].[18] In the other perchlorate ion, the significantly lower temperature factors reflect the semi-co-ordination of O(23) to the mirror related mercury atoms (2·77 Å) and contacts of O(21) with mercury atoms related by a *c* unit translation (2·93 and 3·04 Å, Figure 2), resulting in more normal dimensions (1·37—1·52 Å).

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