Crystal Structure of Bis-[(1,8-naphthyridine)mercury(I)] Diperchlorate

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by the heavy-atom method and refined by full-matrix least-squares to *R* 0·08 for 1033 observed reflections. Crystals are monoclinic, space group $P2_1/n$, a = 18·639(3), b = 5·164(1), c = 11·224(1) Å, β = 105·95(1)°, with two of the dimeric species in the cell. Hg–Hg is 2·511(1) Å; the naphthyridine ligand is essentially unidentate and coplanar with the mercury and has a very short Hg–N distance of 2·03(2) Å.

MERCURY(I) perchlorate forms complexes of the type $Hg_2L_2(ClO_4)_2$ with unidentate aromatic nitrogen bases, L. Structural studies for those cases where L is 3-chloro- or 4-cyano-pyridine show that co-ordination about the mercury dimer comprises a close axial mercury–nitrogen contact at *ca.* 2·2 Å and longer normal perchlorate oxygen contacts.[1,2] *o*-Phenanthroline, on the other hand, in $Hg_2(o\text{-phen})(NO_3)_2$ behaves as an asymmetrically co-ordinated bidentate ligand, co-ordinating the mercury at longer distances (Hg–N 2·30, 2·48 Å).[3] In this context, it was considered to be of interest to examine the complex formed with 1,8-naphthyridine (napy), a bidentate ligand of small 'bite,' to ascertain its mode of co-ordination. The present complex was prepared by the general method of crystallization from methanolic solution containing equimolar proportions of the ligand and mercury(I) perchlorate with a trace of triethyl orthoformate.[1,2,4]

EXPERIMENTAL

A prismatic crystal 0·25 × 0·43 × 0·18 mm was used for data collection. Unit-cell dimensions were obtained by a least-squares fit of 15 reflections with 2θ *ca.* 50° centred in the counter aperture of a Syntex P$\bar{1}$ diffractometer. A unique data set in the range $2\theta < 100°$ was collected yielding 1047 independent reflections of which 1033 with $I > \sigma(I)$ were considered observed and used in the structure solution and refinement after correction for absorption.

Crystal Data.—$C_{16}H_{12}Cl_2Hg_2N_4O_8$, $M = 860·4$, Monoclinic, $a = 18·639(3)$, $b = 5·164(1)$, $c = 11·224(1)$ Å, $\beta = 105·95(1)°$, $U = 1038·6(3)$ Å^3, $D_m = 2·65(2)$ g cm^{-3}, $Z = 2$, $D_c = 2·75$ g cm^{-3}, $F(000) = 788$. Cu-K_α radiation (monochromatic), $\lambda = 1·5418$ Å, $\mu(\text{Cu-}K_\alpha) = 309·8$ cm^{-1}. Space group $P2_1/n$ (C^5_{2h}, No. 14).

The structure was solved by the heavy-atom method; final refinement stages were by full-matrix least-squares with anisotropic thermal parameters for the non-carbon and -hydrogen atoms being of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}$

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[1] D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, 1973, 893.

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

[3] R. C. Elder, J. Halpern, and J. S. Pond, *J. Amer. Chem. Soc.*, 1967, **89**, 6877.

[4] D. Taylor, Ph.D. Thesis, University of Western Australia, 1972.

TABLE 1

Atomic fractional cell ($\times 10^4$, Hg $\times$ 10^5) and thermal ($\times 10^3$ Å^2) parameters, with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	02330(4)	0207(2)	11570(8)	59(1)	77(1)	22(1)	−3(1)	13(1)	−6(1)
Cl	1138(3)	4674(8)	8443(5)	53(3)	68(3)	35(5)	−2(2)	15(2)	2(2)
O(1)	1075(7)	191(2)	834(1)	68(8)	65(9)	88(9)	−2(6)	34(7)	−3(7)
O(2)	132(1)	537(3)	974(2)	104(13)	88(10)	41(11)	15(8)	21(9)	−16(7)
O(3)	1700(9)	554(3)	793(2)	80(10)	101(11)	77(11)	−23(8)	38(9)	−17(8)
O(4)	0415(8)	584(3)	779(1)	72(9)	96(9)	55(9)	28(9)	−12(7)	−13(8)
N(1)	1376(7)	333(3)	253(1)	45(7)	66(9)	37(7)	1(7)	12(6)	3(7)
N(2)	063(2)	017(3)	303(3)	233(35)	67(13)	142(28)	23(13)	175(28)	44(11)
C(1)	194(1)	521(4)	290(3)	68(7) *					
C(2)	233(1)	579(4)	399(2)	59(5) *					
C(3)	224(1)	434(4)	501(2)	64(5) *					
C(4)	1685(8)	236(3)	476(1)	46(4) *					
C(5)	152(1)	088(4)	564(2)	57(4) *					
C(6)	096(1)	−114(4)	528(2)	59(5) *					
C(7)	0586(9)	−142(4)	400(2)	57(4) *					
C(8)	1288(7)	203(3)	350(1)	38(3) *					

* Isotropic.

$+ U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$]; because of their proximity to the mercury atoms it was considered desirable to refine the nitrogen atoms in this manner. However, the validity of the result must be regarded as very dubious in view of the fact that the ellipsoid for N(2) is very slightly non-positive definite. No hydrogen atoms were included in the refinement since they were indistinct in a final difference map and make little contribution to the scattering. In the final refinement cycle no parameter shift exceeded 0·2σ and refinement terminated at R 0·081 and R' 0·106 [$R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. The weighting scheme used was of the form $w = (\sigma|F_o| + n|F_o|^2)^{-1}$, a value of $n = 11 \times 10^{-4}$ being found appropriate.

TABLE 2

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

(*a*) The cation			
Hg–Hg$^{\mathrm{I}}$	2·511(1)	Hg$^{\mathrm{I}}$–Hg–N(1)	128·2(3)
Hg–N(1)	2·78(1)	Hg$^{\mathrm{I}}$–Hg–N(2)	174·4(5)
Hg–N(2)	2·03(3)	Hg$^{\mathrm{I}}$–Hg–O(4$^{\mathrm{II}}$)	115·6(3)
Hg–O(4$^{\mathrm{II}}$)	2·79(2)	Hg$^{\mathrm{I}}$–Hg–O(1$^{\mathrm{II}}$)	95·8(9)
Hg–O(1$^{\mathrm{III}}$)	2·87(1)	N(1)–Hg–N(2)	54·8(9)
		N(1)–Hg–O(4$^{\mathrm{II}}$)	72·3(4)
N(2)–Hg–O(1$^{\mathrm{III}}$)	83·1(11)	N(1)–Hg–O(1$^{\mathrm{III}}$)	132·6(4)
O(4$^{\mathrm{II}}$)–Hg–O(1$^{\mathrm{III}}$)	72·9(4)	N(2)–Hg–O(4$^{\mathrm{II}}$)	69·4(9)
N(1)–C(1)	1·41(3)	Hg–N(1)–C(1)	164(2)
C(1)–C(2)	1·27(3)	Hg–N(1)–C(8)	85·4(8)
C(2)–C(3)	1·43(3)	Hg–N(2)–C(8)	112(2)
C(3)–C(4)	1·42(3)	Hg–N(2)–C(7)	138(2)
C(4)–C(8)	1·41(2)	N(1)–C(8)–N(2)	107(2)
C(4)–C(5)	1·35(3)	N(1)–C(8)–C(4)	128(1)
C(5)–C(6)	1·46(3)	N(2)–C(8)–C(4)	125(2)
C(7)–N(2)	1·38(4)	N(1)–C(1)–C(2)	129(3)
N(2)–C(8)	1·53(3)	C(1)–C(2)–C(3)	119(2)
C(8)–N(1)	1·33(2)	C(2)–C(3)–C(4)	117(2)
C(6)–C(7)	1·43(2)	C(3)–C(4)–C(8)	116(2)
		C(5)–C(4)–C(8)	120(1)
C(5)–C(6)–C(7)	117(2)	C(3)–C(4)–C(5)	123(2)
C(6)–C(7)–N(2)	128(2)	C(4)–C(5)–C(6)	120(2)
C(1)–N(1)–C(8)	110(2)	C(7)–N(2)–C(8)	108(2)
(*b*) The anion			
Cl–O(1)	1·43(1)	O(1)–Cl–O(2)	108·6(8)
Cl–O(2)	1·44(2)	O(1)–Cl–O(3)	109·8(9)
Cl–O(3)	1·40(2)	O(1)–Cl–O(4)	108·8(8)
Cl–O(4)	1·47(2)	O(2)–Cl–O(3)	110·2(11)
		O(2)–Cl–O(4)	108·7(10)
		O(3)–Cl–O(4)	110·6(10)

Roman numeral superscripts refer to the following equivalent positions:

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

Data processing was carried out by use of a local adaptation of the '*X*-Ray '72' system[5] on a CDC 6200. Scattering factors used were for the neutral atoms,[6] those for Hg and Cl being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[7] Final structure factors are given in Supplementary Publication No. SUP 21182, (6 pp., 1 microfiche).† Final positional and thermal parameters are listed in Table 1, bonds and angles in Table 2.

DISCUSSION

The cell contents (Figure) are comprised of discrete [Hg$_2$(napy)$_2$]$^{2+}$ cations and ClO$_4^-$ anions; as in previous structure determinations[1,2] of Hg$_2$L$_2$(ClO$_4$)$_2$ complexes, we find only one half of the dimeric stoicheiometric unit to be crystallographically independent, the relating symmetry operation in the present case being the inversion centre at the origin. The co-ordination of the naphthyridine ligand to the mercury dimer is asymmetric; while bonding obviously occurs predominantly through N(2) [Hg–N(2) 2·03(3), *cf.* Hg–N(1) 2·78(1) Å], there is clearly some additional interaction with N(1), in spite of its very long contact distance, since the angles Hg–N(2)–C(8) and Hg–N(2)–C(7) are not equal [112(2), *cf.* 138(2)°] and the Hg–Hg–N(2) angle is 174° rather than 180°. The mercury atom is closely coplanar with the naphthyridine ligand. The equation of the ligand plane in orthogonal co-ordinates X, Y, Z where $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$ is $0{\cdot}738X - 0{\cdot}665Y - 0{\cdot}114Z = -0{\cdot}161$; deviations (Å) of atoms from this plane are: N(1) 0·03, N(2) −0·09, C(1) 0·03, C(2) −0·02, C(3) 0, C(4) 0, C(5) −0·02, C(6) 0·02, C(7) 0·05, and C(8) 0·01 (σ 0·04 Å), and Hg 0. However, the inversion-related mercury deviates considerably from this plane by 0·32 Å; clearly,

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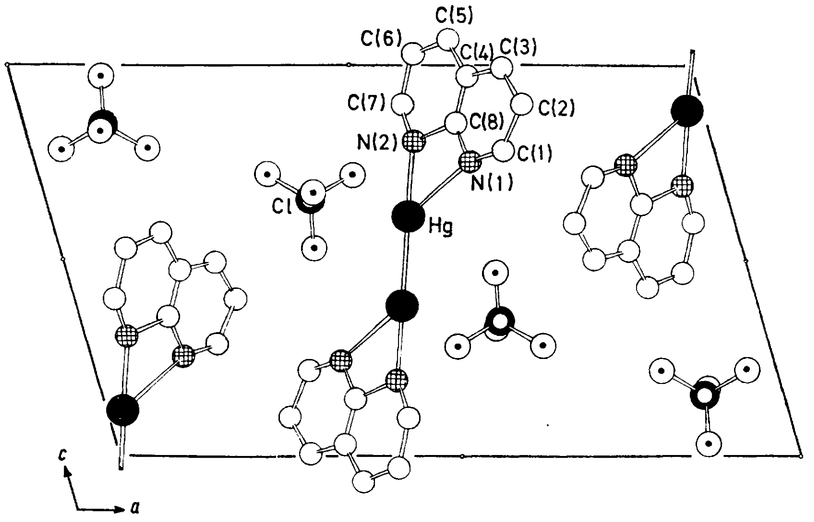
† For details see Notice to Authors, No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[5] '*X*-Ray' system, version of June 1972,' Computer Science Centre, University of Maryland, Technical Report TR 192.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

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

although symmetry requires that the plane and its inverse must be parallel, they are not coincident, so that the cation as a whole is not coplanar, having an appreciable 'step' in the Hg–Hg bond. Clearly also, in its behaviour the napy ligand parallels the unidentate substituted-pyridine ligands more closely than the *o*-phenanthroline ligand, which co-ordinates much more symmetrically, with Hg–N distances more nearly equal and both considerably longer than in the present compound. In fact, the present Hg–N distance is the shortest so far measured (see Table 3).



Unit-cell contents projected down *b*, showing the atom numbering system used in the analysis

TABLE 3

	Hg–N	Hg–Hg	Hg–Hg–N
3-Chloropyridine [a]	2·21(2)	2·487(2)	167·4(7)
4-Cyanopyridine [b]	2·16(3)	2·498(2)	176·0(7)
1,8-Naphthyridine	2·03(2)	2·511(3)	174·4(5)

[a] Ref. 1. [b] Ref. 2.

While any conclusions must be drawn with caution because of the nature of the earlier structure determinations (film) and the general difficulties of accurately determining light-atom geometries in mercury-containing compounds, it is interesting that the decrease in Hg–N distances parallels the observed increase in the Hg–Hg distance; this general observation, however, requires assessment in the light of more accurate structural determinations than those previously reported.

In the previously determined structures, the volume normal to the Hg–Hg axis has been occupied by the perchlorate species, these making long Hg · · · O contacts usually at distances *ca.* 2·9—3·0 Å {although in $[Hg_2(C_6H_4NCl)_2](ClO_4)_2$ there is a closer contact at 2·77(2) Å}; [1] these are generally three in number. In the present case, presumably because of the bulk of the ligand, there are only two such contacts at rather short distances [2·79(2) and 2·87(2) Å]. The perchlorate group is well ordered and regular in its geometry.

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