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Crystal Structure of 4-Cyanopyridinemercury(I) Perchlorate

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The crystal structure of 4-cyanopyridinemercury(I) perchlorate, $[Hg_2(C_6H_4N_2)_2](ClO_4)_2$, has been determined at 298°K by single-crystal X-ray diffraction methods. Solution of the structure by conventional Patterson Fourier heavy-atom techniques, followed by block diagonal least-squares refinement, has resulted in a final conventional R value of 0.104 for 1084 independent, observed, visually estimated reflections. The compound (observed density 2.74 (5) g cm^{-3}, calculated density 2.80 g cm^{-3} for two of the above dimeric formula units in the unit cell) crystallizes in the monoclinic system, space group $P2_1/c$ [a = 5.509 (5), b = 15.11 (1), c = 11.63 (1) Å, β = 98.1 (1)°]. The structure consists of approximately linear $[Hg_2(C_6H_4N_2)]^{2+}$ cations, centrosymmetric about (0, 0, 0) and (0, $^1/_2$, $^1/_2$), and ClO_4^- anions. The mercury–mercury bond length is 2.498 (2) Å. This structure analysis is the first to demonstrate the covalent coordination of nitrogen donor ligands to both mercury atoms of the Hg_2^{2+} dimer.

Introduction

The compounds of mercury(I) are of interest for a number of reasons. They invariably display the presence of the dimeric mercurous Hg_2^{2+} ion, an early and well proven example of metal–metal bonding. The dimeric ion is usually linearly coordinated by the anionic species or the neutral ligand in its coordination complexes.

Among the latter, the number and variety of ligating agents is restricted, most of the well-established examples being those of oxygen donors, such as sulfate,[1] nitrate (hydrate),[2] and other common oxy anions.

Early reports of the crystal structures of the mercurous halides had suggested that in these species, with the linear structure X–Hg–Hg–X, the mercury–mercury distance was strongly dependent on the coordinated halide ion, undergoing a monotonic variation from 2.43 Å in the fluoride, Hg_2F_2, to 2.69 Å in the iodide, Hg_2I_2.[3–5] A complementary effect has been reported in their Raman spectra where the mercury–mercury stretching frequency decreases from 186 cm^{-1} in Hg_2F_2 to 112 cm^{-1} in Hg_2I_2.[6] These observations suggested strongly that the Hg–Hg bond order and length might be expected to vary according to the electronic properties of the ligand in cases of comparable linear coordination. With this in mind and, also, the lack of information on mercury coordination complexes in general, we set out to prepare a series of mercury(I) complexes using mercury(I) perchlorate (because of the limited tendency of the perchlorate ion to coordinate to mercury(I)) and a variety of aromatic nitrogenous bases as ligands, in order to define the compounds formed and to explore the effect of these variations on mercury–mercury bond length. Accordingly, we report here the results of a structural investigation of the complex 4-cyanopyridinemercury(I) perchlorate, $[Hg_2(C_6H_4N_2)_2](ClO_4)_2$.

[During this investigation a redetermination of the structures of the mercury(I) halides has been reported,[7] in which the range of distances reported above has been disproved, the current results suggesting that in the halides the mercury–mercury distances are as follows (Å): Hg_2F_2, 2.507 (1); Hg_2Cl_2, 2.526 (6); Hg_2Br_2, 2.49 (1). In view of the fact that their range of linear substituents produces a comparatively negligible effect on the bond length, it would seem that the mercury–mercury distance is unlikely to vary within a series of complexes of nitrogenous bases in the manner hoped for.]

Experimental Section

The complex was prepared by the slow addition of a solution of 3.0 g (4.46 mmol) of mercury(I) perchlorate tetrahydrate in 20 ml of absolute methanol to a solution of 1.85 g (17.8 mmol) of 4-cyanopyridine (recrystallized from benzene) in 20 ml of the same solvent. After being allowed to stand for 24 hr, the resultant white crystalline solid was filtered off, washed with absolute methanol and ether, and dried under vacuum for 10 hr at room temperature; mp 201°. *Anal.* (Australian Microanalytical Service, CSIRO, Melbourne): Calcd for $HgC_6H_4N_2ClO_4$: Hg, 49.64; C, 17.84; H, 1.00; N, 6.94; Cl, 8.78; O, 15.84. Found: Hg, 49.4; C, 17.90; H, 1.06; N, 6.78; Cl, 8.9; O (difference), 15.96.

The following discussion refers to data obtained using the (multiple-film pack) equiinclination Weissenberg method on a nonintegrating Nonius Weissenberg camera at room temperature (25 ± 3°), using nickel-filtered copper Kα radiation ($\lambda(K\alpha_1)$ 1.5406 Å, $\lambda(K\alpha_2)$ 1.5444 Å, $\lambda(K\bar{\beta})$, 1.3922 Å).[8] Crystals were obtained from the above preparation as monoclinic needles, a being the needle axis and b and c the section diagonals. All data were obtained on a single needle section approximating a prism 0.10 × 0.08 × 0.08 mm, being mounted with the spindle axis parallel to b and then a, respectively. Unit cell dimensions were obtained from zero-layer Weissenberg photographs about b and a, calibrated with aluminum powder ($a_{Al}(25°)$ = 4.0494 Å;[9] a = 5.509 (5), b = 15.11 (1), c = 11.63 (1) Å; β = 98.1 (1)°; U = 958 Å^3). Layers of intensity data were collected in the order $h0l$–$h5l$, $0kl$–$3kl$. During data collection, the crystal gave evidence of slow decomposition in the X-ray beam, becoming discolored and giving, in the latter stages, rather diffuse reflections. However, as no loss of high angle spots in the later layers was observed, this was considered preferable to the use of different crystals, possibly with different characteristics. (However, see below.) The intensities of 1597 independent observed reflections were estimated visually using an intensity strip calibrated with a Joyce Loebl Mark IIIB microdensitometer. Data were corrected for absorption using a program based on the analytical algorithm of ABSCOR,[10] the range of transmission coefficients being 0.061–0.239. After correction for Lorentz and polarization factors using a local program (SCAL1), the data were internally correlated using a local modification of the Hamilton, Rollett, and Sparks

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[1] E. Dorm, *Acta Chem. Scand.*, **23**, 1607 (1969).

[2] D. Grdenić, *J. Chem. Soc.*, 1312 (1956).

[3] D. Grdenić and C. Djordjević, *ibid.*, 1316 (1956).

[4] N. V. Belov and V. I. Mokeeva, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **5**, 13 (1949); *Chem. Abstr.*, **47**, 3648*i* (1953).

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[6] H. Stammreich and T. T. Sans, *J. Mol. Struct.*, **1**, 55 (1967–1968).

[7] E. Dorm, *Chem. Commun.*, 466 (1971).

[8] G. D. Rieck in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 59.

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[10] N. W. Alcock in "Crystallographic Computing," Munksgaard, Copenhagen, 1971, p 271.

Table II

(a) Atomic Fractional (x, y, z) and Orthogonal (X, Y, Z) Coordinates and Isotropic Thermal Parameters

Atom	x	y	z	X	Y	Z	B, Å^2
Hg	0.1335 (3)	0.0366 (1)	0.0821 (1)	0.60	0.55	0.94	
N_1	0.366 (5)	0.108 (2)	0.216 (2)	1.66	1.62	2.49	3.6 (5)
C_2	0.345 (6)	0.093 (2)	0.333 (3)	1.35	1.41	3.83	3.3 (5)
C_3	0.500 (8)	0.137 (3)	0.417 (3)	2.07	2.07	4.80	5.0 (8)
C_4	0.691 (6)	0.192 (2)	0.378 (3)	3.19	2.89	4.36	3.7 (6)
C_5	0.708 (7)	0.203 (2)	0.268 (3)	3.46	3.07	3.09	4.4 (7)
C_6	0.543 (7)	0.155 (3)	0.187 (3)	2.68	2.34	2.15	4.4 (7)
C_7	0.872 (8)	0.236 (3)	0.466 (3)	4.04	3.57	5.37	4.8 (8)
N_2	0.992 (8)	0.278 (3)	0.532 (4)	4.59	4.20	6.13	7.0 (9)
Cl	−0.320 (2)	−0.098 (1)	0.220 (1)	−2.12	−1.48	2.53	4.5 (2)
O_1	−0.161 (7)	−0.023 (2)	0.254 (3)	−1.30	−0.35	2.92	7.2 (8)
O_2	−0.496 (6)	−0.102 (2)	0.303 (3)	−3.23	−1.55	3.49	6.9 (7)
O_3	−0.451 (6)	−0.079 (2)	0.105 (3)	−2.65	−1.19	1.21	6.0 (6)
O_4	−0.188 (7)	−0.179 (3)	0.216 (3)	−1.39	−2.70	2.48	8.4 (9)

(b) Anistropic Thermal Parameters for the Mercury Atom

β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
0.0275 (5)	−0.0044 (4)	−0.0008 (4)	0.0051 (1)	−0.0010 (1)	0.0082 (1)

(c) Root-Mean-Square Amplitudes (Å) and Direction Cosines of Principal Axes of the Mercury Thermal Ellipsoid

U_{ii}	l	m	n	ϕ,[a] deg
0.186	0.812	0.367	0.453	26.3
0.251	−0.364	0.962	−0.097	80.7
0.245	−0.456	−0.086	0.886	65.6

[a] ϕ is the angle between the ith principal axis of the ellipsoid and the Hg′–Hg vector.

algorithm,[11] all reflections being assigned unit weights, to give an arbitrarily scaled set of $|F_o|$, the sets of reflections from upper and lower halves of the nonzero layers about the a axis being scaled independently to assist in offsetting spot-shape distortions.

Structure Determination.—The observed density, $d_m = 2.74$ (5) g cm^{-3}, obtained by flotation in methyl iodide–bromoform, requires four $HgClC_6N_2H_4O_4$ units in the unit cell; in view of the inevitably dimeric nature of the mercurous entity, Hg_2^{2+}, this was taken to imply two $Hg_2(C_6H_4N_2)_2(ClO_4)_2$ units per unit cell, for which d_c is 2.80 g cm^{-3}. This being so, the systematic absences $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$ uniquely determine the space group as $P2_1/c$ (C_{2h}^5, no. 14[12]) and impose the likely requirement that the center of the Hg–Hg bond is a special position. This was confirmed from a three-dimensional unmodified Patterson function computed from all data, the coordinates of the chlorine and mercury atoms being thereby obtained. Two cycles of block diagonal (3×3, 6×6) least-squares refinement of the positional and isotropic thermal parameters led to a conventional R value of 0.32 ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$). A difference Fourier synthesis computed at this stage located all remaining nonhydrogen atoms, and refinement of positional and isotropic thermal parameters of all atoms gave, after four further cycles, an R value of 0.17, the mercury temperature factor being 3.7 Å^2. The structure was then further refined, introducing a weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$,[13] the function $\Sigma w(|F_o| - |F_c|)^2$ being minimized and a and b adjusted as refinement proceeded; anisotropic thermal parameters of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hl\beta_{13} + kl\beta_{23} + hk\beta_{12})]$ were introduced for the mercury atom only. Reflections with intensities close to background which were likely to be of low accuracy were eliminated from the least-squares refinement using the requirement that for inclusion $|F_o| < |F_c|$, accounting for 292 reflections being regarded as "unobserved." After six further cycles of refinement, R was 0.118. Agreement analysis at this stage showed that the R value for the layer $3kl$ was 0.155. As the data from this layer were the most seriously affected by crystal decomposition, they were eliminated from the data set accounting for 221 further reflections, the procedure being further justified by the fact that the estimated standard deviations of all parameters were lowered. Refinement of the structure continued to a final R of 0.104 for a total of 1084 observed reflections.

Final weighting scheme constants were $a = 42.7$, $b = 0.0058$. The final "weighted R," $R' = (\Sigma(||F_o| - |F_c||)^2/\Sigma w|F_o|^2)^{1/2}$, was 0.138. [On this final data set, the mercury thermal parameters were restored to being isotropic; refinement to convergence gave $R = 0.168$ and $R' = 0.219$. On the basis of a ratio test, it was concluded that the anisotropic thermal parameters derived were significant.[14]] At convergence, positional parameter shifts for the mercury and the lighter atoms were all less than 0.05 estimated standard deviation; anisotropic thermal parameter shifts for the mercury atom were of the order of 1 esd and isotropic thermal parameter shifts for the remaining atoms were less than 0.1 esd. A final difference Fourier located no peaks greater than 0.3 of a carbon atom, the majority being concentrated in a region less than 2 Å from the mercury atom. There was no evidence for disorder in the structure and, in particular, all atoms of the perchlorate ion were well defined. Refinement programs were the local SFLS1,2 (A. I. M. Rae).

Scattering factors employed were those of Cromer and Waber[15] for monovalent mercury and zerovalent chlorine, oxygen, nitrogen, and carbon, these being considered most suitable for the treatment of heavy atoms.[16] The mercury scattering curve was corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) using the values of Cromer.[17] Final observed and calculated structure factors ($R = 0.104$; 1084 observed reflections) are given in Table I.[18]

Final atomic coordinates and temperature factors are given in Table II with estimated standard deviations in the final digit in parentheses; the latter, being the derivative of a block diagonal least-squares procedure, should be treated with caution as they are likely to be underestimates. Atomic positions are also referred to a set of orthogonal coordinates (X, Y, Z) defined by $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. For the mercury atom, root-mean-square amplitudes of vibration in ångströms are given along the three principal axes of the thermal ellipsoid, together with the orientations of the latter relative to the above orthogonal set of axes. Atomic designations in this and subsequent tables and discussion are derived from the definition of Figure 2.

Interatomic distances and angles, together with estimated standard deviations (see above), were derived using the BONDSCAN program of Pippy and Ahmed[19] and are given in Table III.

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(11) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Crystallogr.*, **18**, 129 (1965).

(12) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965.

(13) D. W. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Elmsford, N. Y., 1965, p 114.

(14) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(15) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

(16) D. T. Cromer, *ibid.*, **19**, 224 (1965).

(17) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(18) Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1639. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(19) M. E. Pippy and F. R. Ahmed, Division of Pure and Applied Physics, National Research Council, Ottawa, Canada, Program NRC-12.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)[a]

	Distances		
$Hg-Hg'$	2.498 (2)	N_1-C_2	1.40 (4)
$Hg-N_1$	2.16 (3)	N_1-C_6	1.30 (5)
$Hg-O_1$	2.89 (4)	C_2-C_3	1.37 (5)
$Hg-O_3'$	3.04 (3)	C_3-C_4	1.46 (5)
$Hg-O_3''$	2.86 (3)	C_4-C_5	1.31 (5)
$Hg-N_2''$	2.94 (4)	C_5-C_6	1.42 (5)
		C_4-C_7	1.49 (5)
$Cl-O_1$	1.45 (4)	C_7-N_2	1.13 (6)
$Cl-O_2$	1.47 (4)		
$Cl-O_3$	1.46 (3)		
$Cl-O_4$	1.42 (4)		
	Angles		
$Hg'-Hg-N_1$	176.0 (7)	$Hg-N_1-C_2$	120 (2)
$Hg'-Hg-O_1$	94 (1)	$Hg-N_1-C_6$	118 (2)
$Hg'-Hg-O_3'$	83 (1)	$C_6-N_1-C_2$	121 (3)
$Hg'-Hg-N_2''$	99 (1)	$N_1-C_2-C_3$	119 (3)
$Hg'-Hg-O_3''$	100 (1)	$C_2-C_3-C_4$	117 (3)
$N_2''-Hg-O_3''$	142 (1)	$C_3-C_4-C_5$	122 (3)
O_1-Hg-O_3'	174 (1)	$C_4-C_5-C_6$	117 (3)
O_1-Cl-O_2	107 (2)	$C_5-C_6-N_1$	123 (3)
O_1-Cl-O_3	107 (2)	$C_2-C_4-C_7$	119 (2)
O_1-Cl-O_4	113 (2)	$C_5-C_4-C_7$	119 (3)
O_2-Cl-O_3	109 (2)	$C_4-C_7-N_2$	172 (4)
O_2-Cl-O_4	112 (2)		
O_3-Cl-O_4	109 (2)		

[a] The atomic designation refers to Figure 2. Atom Hg′ is related to Hg(x, y, z) by ($\bar{x}$, $\bar{y}$, $\bar{z}$). Atom O_3' is related to O_3(x, y, z) by ($\bar{x}$, $\bar{y}$, $\bar{z}$). Atom O_3'' is related to O_3(x, y, z) by ($1 + x$, y, z). Atom N_2'', is related to N_2(x, y, z) by ($x - 1$, $^1/_2 - y$, $z - {}^1/_2$).

TABLE IV

DISTANCES (Å) OF ATOMS FROM THE LEAST-SQUARES BEST PLANE: $-0.621X + 0.782Y - 0.049Z = 0.083$

Hg	−0.07	C_4[a]	−0.01	N_2[a]	0.05
N_1[a]	0.03	C_5[a]	0.02	O_1	0.31
C_2[a]	−0.01	C_6[a]	−0.02	O_3'[b]	−0.74
C_3[a]	0.01	C_7[a]	−0.06		

[a] Atoms used in plane calculation. [b] Relates to O_3(x, y, z) by the transformation ($\bar{x}$, $\bar{y}$, $\bar{z}$).

A least-squares plane was computed through the ligand, together with deviations in ångströms in the orthogonal coordinate system (X, Y, Z) defined above, and is given in Table IV. Computation was carried out on the DEC PDP10 computer at the University of Western Australia, using programs kindly made available by E. N. Maslen and B. N. Figgis.

Description of Structure

The essential structure features of 4-cyanopyridinemercury(I) perchlorate are summarized in Tables III and IV and depicted in Figures 1 and 2. The crystals are composed of approximately planar, dimeric $[Hg_2(C_6H_4N_2)_2]^{2+}$ cations and tetrahedral perchlorate anions. Only half of the cation is crystallographically independent, the remaining half being related by a center of symmetry at the midpoint of the mercury–mercury bond. The cation is approximately planar (*vide infra*) and is oblique to all three crystallographic axes. There is no crystallographic symmetry imposed on the perchlorate anions.

The mercury atom (Hg) has a distorted octahedral ligand environment, but only the centrosymmetric mercury atom (Hg′) and the pyridine ring nitrogen atom can be considered as being covalently bonded. A linear covalent coordination (Hg′–Hg–N = 176°) together with four weak interactions approximately perpendicular to the bonding axis is a characteristic coordination found in most mercury compounds.[20] The mercury–mercury bond length, 2.498 (2) Å, is in agreement with established values for the mercurous ion (see Table V) and reflects the constancy of this bond length despite different ligands.

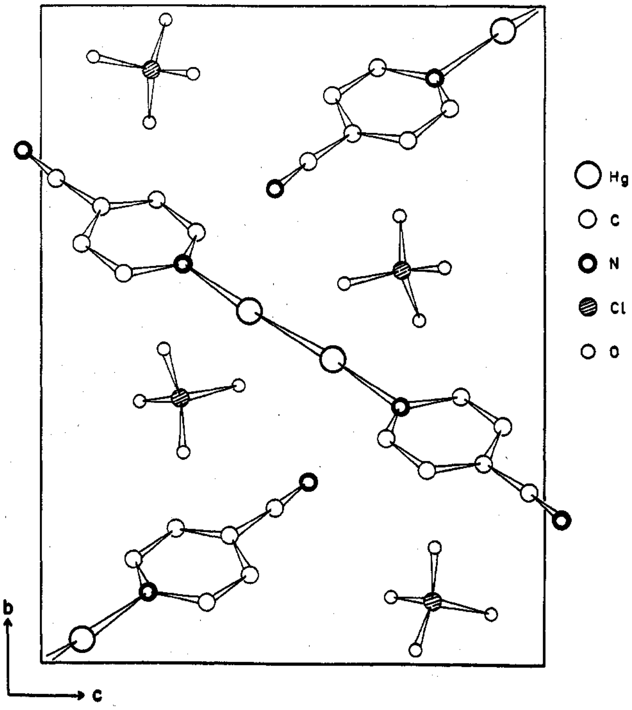

Figure 1.—A projection of the unit cell of 4-cyanopyridinemercury(I) perchlorate on the *bc* plane.

In this complex, the 4-cyanopyridine molecule coordinates through the more basic ring nitrogen rather than the nitrile nitrogen atom. The mercury–nitrogen ($Hg-N_1$) bond length of 2.16 (3) Å, although not of high precision, is significantly different from the mercury–nitrogen distances of 2.30 (4) and 2.48 (4) Å found in the structure of Hg_2(*o*-phen)$(NO_3)_2$.[21] In the latter compound, the bidentate *o*-phenanthroline ligand is approximately symmetrically positioned with respect to the axis of the mercury dimer and hence is unlikely to coordinate as strongly as a monodentate nitrogen donor ligand occupying the axial site. Rather, the mercury–nitrogen bond length in 4-cyanopyridinemercury(I) perchlorate can be favorably compared with mercury(II)–nitrogen distances of 2.05–2.11 Å[22] and mercury(I)–oxygen bond lengths ranging from 2.08 (5) Å in $[Hg_2$(*o*-phthalate)$]$[23] to 2.24 (2) Å in Hg_2SO_4,[1] these bond lengths being for axial donor ligands only.

The accuracy of bond lengths and angles for the 4-cyanopyridine ligand is low due mainly to the domination of the X-ray scattering by the mercury atoms. They are, however, in general agreement with the results of a recent determination of the structure of that molecule.[24] The equation of a best least-squares plane for the ligand and the atomic deviations are given in Table IV. Because of the fact that the cation is centro-

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[20] D. Grdenić, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965).

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

[22] D. Breitinger and K. Brodersen, *Angew. Chem.*, **82**, 379 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 357 (1970).

[23] B. Lindh, *Acta Chem. Scand.*, **20**, 553 (1966).

[24] M. Laing, N. Sparrow, and P. Sommerville, *Acta Crystallogr., Sect. B*, **27**, 1986 (1971).

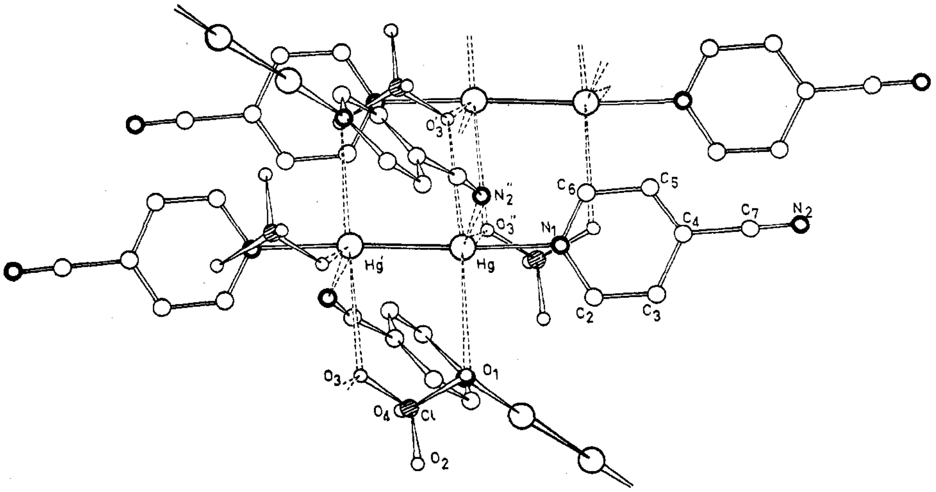

Figure 2.—A view of the structure projected onto the plane of the ligand. The dashed lines do not represent bonds but indicate the positions of next nearest neighbor atoms.

TABLE V

MERCURY–MERCURY BOND LENGTHS IN SOME MERCURY(I) COMPOUNDS

Compd	Hg–Hg distance, Å	Ref
Hg_2F_2	2.507 (1)	7
Hg_2Cl_2	2.526 (6)	7
Hg_2Br_2	2.49 (1)	7
$[Hg_2(H_2O)_2](NO_3)_2$	2.54 (1)	2
$[Hg_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	2.50 (1)	*a*
$[Hg_2(BrO_3)_2]$	2.507 (6)	*b*
Hg_2SO_4	2.500 (3)	1
Hg_2SeO_4	2.51 (1)	1
Hg_2(*o*-phthalate)	2.519 (4)	23
Hg_2(*o*-phen)$(NO_3)_2$	2.516 (7)	21
$[Hg_2(C_6H_4N_2)_2](ClO_4)_2$	2.498 (2)	This work

[a] G. Johansson, *Acta Chem. Scand.*, **20**, 553 (1966). [b] E. Dorm, *ibid.*, **21**, 2834 (1967).

symmetric and in view of only a small deviation of the origin from the plane, the entire cation can be described as being approximately planar.

The geometry of coordination other than the linear N'–Hg'–Hg–N arrangement serves to complete a distorted octahedron about each mercury atom. However, this secondary coordination is best described in terms of electrostatic interactions since the mercury–oxygen distances of 2.86 (3), 2.89 (4), and 3.04 (3) Å and the mercury–nitrogen (N_2'') distance of 2.94 (4) Å are comparable to the sum of the appropriate van der Waals radii being 2.9 and 3.0 Å, respectively.[20,25] All other mercury–oxygen distances are greater than 3.5 Å. It is interesting to note that the perchlorate ion spans the mercury dimer and that, presumably, it is the weak Hg–O_1 and Hg'–O_3 interactions which preclude any possible disorder of the ion. One of the oxygen atoms of each perchlorate ion (O_3, O_3', O_3'', . . .) bridges mercury atoms of different cations. These neighboring dimeric cations pack in a stepwise fashion in parallel planes 3.42 Å apart, this distance corresponding very well to the "thickness" of an aromatic molecule.[25] (There are in fact two sets of planes related by the 2_1 symmetry operation.) Although the cations do not stack exactly above one another but are offset, it would seem that this mode of packing is the cause of the approximate planarity of the $[Hg_2(C_6H_4N_2)_2]^{2+}$ cation rather than any torsional rigidity of the metal–metal bond. The latter would imply a multiple mercury–mercury bond which is difficult to formulate electronically in view of the filled $5d^{10}$ electron shell for each of the mercury atoms.

The perchlorate anion is undistorted, within experimental error, from its expected tetrahedral angle and the average chlorine–oxygen bond length of 1.45 (1) Å is in good agreement with other observed values.[26] This is in contrast to perchloratometal complexes which invariably exhibit distortion of the coordinated perchlorate ion from its idealized T_d symmetry.[27] Thus, it can be inferred that in 4-cyanopyridinemercury(I) perchlorate covalent bonding between the mercury atom and the oxygen atoms of the perchlorate ion is minimal.

The thermal vibration of the mercury atom is decidedly anisotropic, the amplitude of vibration along the dimer axis being only about 70% of the amplitudes of vibration perpendicular to the mercury–mercury bond. This confirms previous similar observations.[1,21]

Discussion

One of the first substantial indications that mercury(I) could form stable covalent complexes with nitrogen bases rather than undergoing disproportionation was the determination of the formation constant for the complex $[Hg_2(\text{aniline})_2]^{2+}$.[28] Although the complex was not isolated, it was suggested that it may be possible, at least in solution, to detect complexes of mercury(I) with nitrogen donors of low basicity. It is well known that many amines including pyridine (pK_a = 5.21)[29] cause disproportionation of the mercury(I) dimer to mercury(II) and mercury metal.[22] However, by introducing an electron-withdrawing substituent in the 4 position of the pyridine nucleus, the donor ability of the ring nitrogen is decreased. Thus, it may be the isolation of a mercury(I) complex of 4-cyanopyridine (pK_a = 1.86)[29] is an important delineation of the factors affecting the stability of mercury(I) coordination com-

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pounds, and the structure determination is first to demonstrate the ability of Hg_2^{2+} to coordinate covalently nitrogen donor ligands to both mercury atoms.

The mercury–nitrogen ($Hg–N_1$) bond distance of 2.16 (3) Å in this complex indicates that the mercurous ion, Hg_2^{2+}, is capable of forming strong coordinate bonds. The distance is only slightly greater than the normal mercury(II)–nitrogen bond lengths,[22] despite the reduced nuclear charge for the lower oxidation state of mercury and the weak σ-donor ability of the ligand. However, the inductive effect of the substituent in 4-cyanopyridine is expected to make the pyridine nucleus a good π acceptor. Therefore, in the absence of appreciable $N \rightarrow Hg$ σ bonding, it is possible that π bonding ($d\pi \rightarrow \pi^*$) stabilizes the mercury–nitrogen bond, resulting in a normal bond distance. (Wong and Brewer have employed a similar argument to explain the strength of the coordination bond in the zinc(II)–4-cyanopyridine complex.[30])

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The Crystal and Molecular Structure of Tris(dimethylhydrazino)bis(phosphine oxide), $OP(NCH_3NCH_3)_3PO$

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The structure of tris(dimethylhydrazino)bis(phosphine oxide), $OP(NCH_3NCH_3)_3PO$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $C2/c$ or Cc with four molecules in a unit cell of dimensions $a = 9.757$, $b = 10.068$, $c = 13.175$ Å, and $\beta = 104.98°$. Full-matrix, least-squares refinement has led to a final value of the unweighted R index (on structure factors in group $C2/c$) of 0.056 for the 1781 reflections for which the observed intensity $I > 3\sigma(I)$. The structure is fully disordered so that the molecular symmetry, which is 32, appears to be $\bar{3}m$. All P, O, and C atoms in one molecule are nearly at the same positions as the corresponding atoms in the inverse molecule at the same lattice site; accordingly only average positions for these atoms have been determined. Each molecule consists of two OP units joined by three NCH_3NCH_3 bridges. The P–N bond length (1.66 Å) and the geometry about the nitrogen are discussed in terms of $d\pi$–$p\pi$ bonding. The 2.82-Å separation of the two phosphorus atoms may indicate a weak bond between them.

Introduction

The stereochemistry of phosphorus–nitrogen compounds is of current interest[1-3] because of the possible formation of $p\pi$–$d\pi$ bonds between these two atoms. Structures of several cyclic P^V–N compounds[4-7] have been published and while only a few compounds containing the P^{III}–N unit have been examined,[2,3,8-11] the number is growing rapidly. Unfortunately, with the single exception of the $F_2PN(CH_3)_2$[9] and $B_4H_8F_2PN(CH_3)_2$[8] pair there are no data available which permit structural comparisons between similar compounds in which the effect of oxidation state, lone-pair electrons, and neighboring groups on the P–N linkage can be detected.

Recently, $P(NCH_3NCH_3)_3P$ was studied by X-ray diffraction.[2] Since we had already begun a structural investigation of its crystalline dioxide, $OP(NCH_3NCH_3)_3PO$, first reported by Payne, Noth, and Henniger,[12] the opportunity presented itself to examine the effects of increasing oxidation state and of coordination of the phosphorus lone pair on the structure of a P–N unit incorporated in a sterically constrained cage. $OP(NCH_3NCH_3)_3PO$ was of further interest in view of the current theoretical studies on the PO bond[13-15] and because of the suggestion that in similar S–N compounds, coordination of the nonbonding pairs on sulfur eliminates the influence of these lone pairs on physical properties, allowing effects arising from d-orbital participation to be more easily observed.[16]

Experimental Section

$OP(NCH_3NCH_3)_3PO$[12] was prepared by air oxidation of $P(NCH_3NCH_3)_3P$ in pyridine solution. Pale yellow prismatic crystals were obtained by recrystallization from the same solvent by Dr. E. Putkey. An equant prismatic crystal approximately 0.040 cm on a side was sealed in a capillary tube with a wall thickness of 0.001 cm. Preliminary investigations using a Syntex $P\bar{1}$ autodiffractometer indicated that the crystals were monoclinic and had systematic absences corresponding to the space groups Cc and $C2/c$. Cell dimensions at 22° were found

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