Crystal and Molecular Structure of (2,2′-Bipyridyl)methylmercury(II) Nitrate, a Complex with Irregular Three-co-ordination

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Crystals of the title compound are triclinic, with $a = 10.299(5)$, $b = 9.289(5)$, $c = 6.841(4)$ Å, $\alpha = 88.98(4)$, $\beta = 105.57(5)$, $\gamma = 84.81(4)°$, $Z = 2$, and space group $P\bar{1}$. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares techniques to R 0.061 for 1 325 reflections collected by diffractometer. The complex has a planar C,Hg,N,N′ group with unsymmetrically chelated 2,2′-bipyridyl and three-co-ordinate mercury: Hg–C 2.07(5), Hg–N 2.24(3), and Hg–N′ 2.43(3) Å; C–Hg–N 164(1), C–Hg–N′ 126(1), and N–Hg–N′ (chelate angle) 69(1)°. The nitrate ion is regular and unco-ordinated.

THE co-ordination chemistry of methylmercury(II) compounds is restricted almost entirely to linear geometry with a co-ordination number of two for mercury.[1–8] Apart from $[\mathrm{MeHgO(SiMe_3)}]_4$ which has distorted tetrahedral geometry for mercury,[9] crystallographic studies of $\mathrm{MeHg^{II}}$ compounds show linear,[1–4] or almost linear [168.1—177.6(0.9)°],[1,5–8] geometry for mercury with co-ordination number two, although several structures have additional potential donor atoms at distances from mercury slightly lower (max. *ca.* 0.2 Å) [6,7] than the sum of van der Waals radii.[1,4–8] Spectroscopic studies indicate weak additional co-ordination in the solid state for some $\mathrm{MeHg^{II}}$ compounds,[10] and stability constant studies of $\mathrm{MeHg^{II}}$ with some potential bidentate ligands, *e.g.* 2,2′-bipyridyl, 1,10-phenanthroline, and 8-hydroxyquinoline, suggest chelation to give three-co-ordinate mercury in aqueous solution.[11] For unidentate ligands giving co-ordination numbers greater than two in solution, both physical [12–15] and spectroscopic [12,16,17] data are consistent with a dominant linear, or almost linear, moiety with additional weak interactions, *e.g.* stepwise stability constants for $\mathrm{MeHgX}_n{}^{(1-n)+}$ [$n > 1$, $\mathrm{X = Cl^-}$ (refs. 13, 14), $\mathrm{Br^-}$ (ref. 14), and $\mathrm{SCN^-}$ (ref. 15)] are very small, and Raman, i.r., and n.m.r. studies of complex formation of MeHgSCN with $\mathrm{SCN^-}$ indicate that the mercury hybridization remains essentially unchanged.[16]

The complex $[\mathrm{MeHg(bipy)}][\mathrm{NO_3}]$ (bipy = 2,2′-bipyridyl) was isolated in crystalline form but it was not known whether bipy was present as a uni- or bi-dentate ligand.[18] As solution studies indicated that bipy may be co-ordinated to $\mathrm{MeHg^{II}}$ in aqueous solution,[11] we determined the crystal structure of this complex.[19]

EXPERIMENTAL

The complex was prepared by the reported method [18] and crystals grown from methanol.

Crystal Data.—$\mathrm{C_{11}H_{11}HgN_3O_3}$, $M = 433.82$, Triclinic, $a = 10.229(5)$, $b = 9.289(5)$, $c = 6.841(4)$ Å, $\alpha = 88.98(4)$, $\beta = 105.57(5)$, $\gamma = 84.81(4)°$, $U = 623.0$ Å^3, $D_\mathrm{m} = 2.39$ g cm^{-3} (by flotation), $Z = 2$, $D_\mathrm{c} = 2.31$ g cm^{-3}, $F(000) = 404$. Space group $P1$ or $P\bar{1}$ shown by the subsequent successful refinement to be the centrosymmetric space group $P\bar{1}$ (No. 2, C_i^1). Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 125.9 cm^{-1}.

Intensity Measurements.—Intensity data were collected from one crystal with dimensions *ca.* 0.10 × 0.10 × 0.14 mm (optimum size 0.15 mm) with a Philips PW 1100 diffractometer. Of 1 741 reflections of the unique data set collected out to 2θ(Mo-K_α) 46°, 416 were considered unobserved [$I < 3\sigma(I)$] and were not used in subsequent calculations. Three standard reflections monitored at 1 h intervals showed no significant variations in intensity. Data were collected by the ω scan technique with a symmetric scan width of $\pm0.55°$ in ω plus an allowance for dispersion, with a scan rate of 0.02° s^{-1}. The Mo-K_α radiation was monochromatized with a flat graphite monochromator, and no reflection was sufficiently strong to require the insertion of an attenuation filter. Data were processed with a programme written specifically for the PW 1100 diffractometer.[20] Neither extinction nor absorption corrections were applied.

Structure Determination and Refinement.—In the least-squares calculations the function minimized was $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$. The Patterson synthesis enabled location of the mercury atom by standard methods, and one cycle of full-matrix least-squares refinement of positional parameters and an isotropic thermal parameter gave R 0.195. All non-hydrogen atoms were located in the subsequent difference-Fourier synthesis; several cycles of full-matrix refinement with all atoms having isotropic thermal para-

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meters, plus several cycles of block-diagonal refinement with mercury anisotropic and the non-hydrogen atoms isotropic led to R 0.089 and R' 0.094 {where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}. A difference-Fourier map revealed approximate positions of hydrogen atoms, and their positions were idealized assuming C–H 1.05 Å and approximate trigonal geometry at the carbon atom. Hydrogen atoms were assigned isotropic thermal parameters 1 Å^2 greater than the equivalent isotropic thermal parameter of the atom to which they are attached. Finally, several cycles of block-diagonal refinement with all non-hydrogen atoms being refined with anisotropic thermal parameters, and no refinement of hydrogen atom parameters, converged with R (observed reflections) 0.061, R' 0.069, and R (all reflections) 0.084, R' 0.074. The final difference-Fourier had no major characteristics >0.5 eÅ^{-3}, this being in the vicinity of the mercury atom.

TABLE 1

Final fractional co-ordinates (× 10^4) and anisotropic thermal parameters * for non-hydrogen atoms, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	2 119(2)	2 315(2)	2 905(2)	360(6)	476(7)	444(7)	−165(5)	149(5)	−25(5)
C(1)	549(40)	1 218(50)	3 372(74)	32(19)	70(27)	82(30)	−11(18)	6(19)	48(23)
C(2)	4 421(32)	4 256(32)	2 627(49)	30(15)	16(13)	34(16)	−10(11)	10(13)	−6(12)
C(3)	5 701(31)	4 578(37)	2 612(51)	17(14)	40(18)	38(17)	6(12)	13(13)	−5(14)
C(4)	6 681(38)	3 479(42)	2 661(51)	46(19)	51(20)	27(17)	−17(16)	17(15)	−6(14)
C(5)	6 430(34)	2 087(49)	2 748(52)	16(14)	91(28)	24(16)	10(16)	1(12)	−7(17)
C(6)	5 135(37)	1 754(43)	2 783(52)	35(18)	60(22)	24(16)	17(16)	−1(14)	−14(15)
C(2′)	3 284(35)	5 379(36)	2 411(49)	38(17)	33(17)	27(16)	−3(14)	11(14)	−5(13)
C(3′)	3 404(34)	6 805(39)	2 113(54)	29(16)	42(18)	39(18)	−11(14)	15(14)	−10(14)
C(4′)	2 299(45)	7 846(42)	1 892(58)	61(23)	45(20)	39(20)	−16(18)	15(18)	−12(16)
C(5′)	1 088(41)	7 354(42)	1 993(61)	43(20)	44(20)	51(22)	9(16)	12(17)	−8(17)
C(6′)	1 032(38)	5 883(42)	2 335(58)	36(18)	47(20)	43(20)	−8(15)	8(15)	−11(16)
N(1)	4 142(39)	2 916(35)	2 658(39)	34(14)	67(18)	16(12)	−7(13)	7(11)	1(12)
N(1′)	2 094(27)	4 921(28)	2 551(42)	30(13)	30(13)	40(15)	9(10)	16(11)	−2(11)
N(2)	2 708(30)	1 999(33)	8 143(47)	30(13)	48(16)	49(17)	−12(12)	7(12)	−1(13)
O(1)	3 630(26)	1 698(31)	7 273(45)	39(13)	62(16)	73(18)	−13(12)	34(13)	−6(13)
O(2)	2 340(30)	978(31)	9 048(45)	64(17)	57(16)	64(17)	−31(13)	28(14)	−6(13)
O(3)	2 192(29)	3 187(34)	8 140(57)	38(14)	61(17)	120(26)	−4(12)	29(16)	3(16)

* Anisotropic thermal parameters are of the form: $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$, and are × 10^2 for Hg, × 10 for the other atoms.

TABLE 2

Calculated co-ordinates (× 10^4) and isotropic thermal parameters for hydrogen atoms, numbered according to the carbon atoms to which they are attached

	x/a	y/b	z/c	B
H(3)	5 933	5 673	2 560	5.9
H(4)	7 678	3 712	2 633	6.3
H(5)	7 212	1 234	2 775	7.3
H(6)	4 943	640	2 872	6.9
H(3′)	4 360	7 137	2 056	6.5
H(4′)	2 382	8 974	1 675	7.7
H(5′)	197	8 107	1 783	7.9
H(6′)	97	5 547	2 520	7.1

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21754 (9 pp., 1 microfiche).* Final parameters for all atoms are listed in Tables 1 and 2, together with their estimated standard deviations, which were derived from the inverse least-squares matrix. Atomic scattering factors for neutral atoms were taken from ref. 21.

Calculations.—All calculations were performed on the Monash University CDC 3200 computer. The major programs used during the refinement were modified versions of ORFLS [22] and the Fourier program of White.[23] Figure 1 was drawn by use of the program ORTEP.[24]

RESULTS AND DISCUSSION

Aspects of the molecular geometry are given in Tables 3 and 4, and two different views of the molecule are in Figures 1 and 2.

TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

(*a*) Mercury environment

Hg–C(1)	2.07(5)	Hg···O(1)	2.99(3)
Hg–N(1)	2.24(3)	Hg···O(2′)	2.99(3)
Hg–N(1′)	2.43(3)		

(*b*) 2,2′-Bipyridyl group

C(2)–N(1)	1.30(4)	C(2′)–N(1′)	1.35(5)
C(2)–C(3)	1.37(5)	C(2′)–C(3′)	1.36(5)
C(3)–C(4)	1.36(5)	C(3′)–C(4′)	1.39(5)
C(4)–C(5)	1.34(6)	C(4′)–C(5′)	1.38(6)
C(5)–C(6)	1.39(6)	C(5′)–C(6′)	1.39(6)
C(6)–N(1)	1.40(5)	C(6′)–N(1′)	1.32(5)
C(2)–C(2′)	1.47(5)		

(*c*) Nitrate group

N(2)–O(1)	1.26(5)	N(2)–O(3)	1.18(4)
N(2)–O(2)	1.26(5)		

The crystal structure is composed of $[\mathrm{MeHg(bipy)}]^+$ cations and nitrate anions. There are two nitrate oxygen atoms 2.99(3) Å [O(1) and O(2′)] from mercury,

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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one above and one below the $[MeHg(bipy)]^+$ group (Figure 1). There is no evidence of nitrate co-ordination: the nitrate ion is regular (within 1σ in bond lengths and angles) and the mercury–oxygen distances correspond closely to the sum of van der Waals radii, 2.9 [Hg 1.5 (ref. 1), O 1.4 Å (ref. 25)], or 3.13 Å using an upper limit [1] of 1.73 Å for the radius of mercury.

TABLE 4

Angles (°), with estimated standard deviations in parentheses

(*a*) About mercury			
C(1)–Hg–N(1)	164(1)	N(1)–Hg–N(1′)	69(1)
C(1)–Hg–N(1′)	126(1)		
(*b*) 2,2′-Bipyridyl group			
C(2)–N(1)–Hg	122(2)	C(2′)–N(1′)–Hg	115(2)
C(6)–N(1)–Hg	115(2)	C(6′)–N(1′)–Hg	127(2)
C(3)–C(2)–N(1)	121(3)	C(3′)–C(2′)–N(1′)	121(3)
C(3)–C(2)–C(2′)	122(3)	C(3′)–C(2′)–C(2)	123(3)
C(2′)–C(2)–N(1)	117(3)	C(2)–C(2′)–N(1′)	116(3)
C(2)–C(3)–C(4)	119(3)	C(2′)–C(3′)–C(4′)	121(3)
C(3)–C(4)–C(5)	122(4)	C(3′)–C(4′)–C(5′)	117(4)
C(4)–C(5)–C(6)	120(4)	C(4′)–C(5′)–C(6′)	120(4)
C(5)–C(6)–N(1)	117(3)	C(5′)–C(6′)–N(1′)	123(4)
(*c*) Nitrate group			
O(1)–N(2)–O(2)	118(3)	O(2)–N(2)–O(3)	120(3)
O(1)–N(2)–O(3)	122(3)		

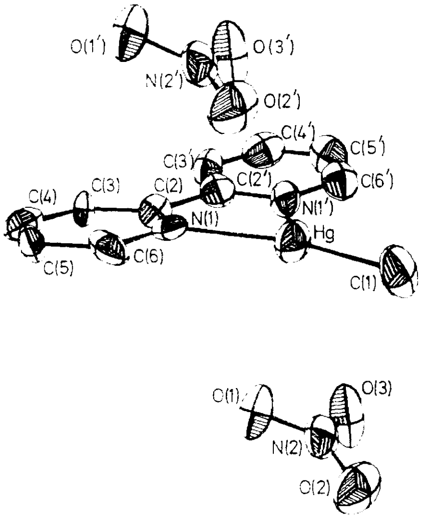

FIGURE 1 Structure of $[MeHg(2,2'\text{-bipyridyl})][NO_3]$ viewed along [010] showing the position of nitrate ions near the cation

The atoms C(1), Hg, N(1), and N(1′) are essentially coplanar as the mercury atom is 0.060(1) Å out of the plane defined by atoms C(1), N(1), and N(1′). The equation for the plane, referred to the orthogonal set of axes *a*,*b*,*c** and with *X*,*Y*,*Z* as co-ordinates in Å, is: $-0.073\,5X - 0.113\,3Y - 0.990\,8Z + 2.341\,7 = 0$.

The mercury–carbon bond distance, 2.07(5) Å, is similar to those found in $MeHg^{II}$ amino-acid complexes having mercury bonded to a neutral amine nitrogen: 2.165(6) Å in $MeHg^+–NH_2·CH(CO_2^-)·CMe_2·S·HgMe$,[6] and 2.11(5) Å in $MeHg^+–NH_2·CH(CO_2^-)·CH_2·CH_2·SMe$.[7] Both nitrogen atoms are bonded to mercury, the distances Hg–N(1) and Hg–N(1′) being 0.76 and 0.57 Å less than the sum of van der Waals radii, 3.0 Å [N 1.5 Å (ref. 25)]. The shorter mercury–nitrogen bond in the 2,2′-bipyridyl complex [2.24(3) Å] is similar to that in $MeHg^+–NH_2·CH(CO_2^-)·CMe_2·S·HgMe$ [6] which has similar non-linear geometry with one additional weak intramolecular interaction [C–Hg–N 168.1°, Hg–N 2.216(5), Hg · · · O 2.708(4) Å]. The longer mercury–nitrogen bond, 2.43(3) Å, is similar to those found in mercury(II) complexes of 2,2′-bipyridyl and 1,10-phenanthroline with higher co-ordination numbers for mercury, *e.g.* 2.373(9) and 2.399(8) Å in $[HgBr_2(bipy)]_2$ (five-co-ordinate) [26] and 2.42(2)—2.52(2) Å in $[Hg(SCN)_2(phen)_2]$ (six-co-ordinate).[27] In addition to mercury–nitrogen bond lengths the angular distribution of bonds involving mercury is also irregular (Figure 2).

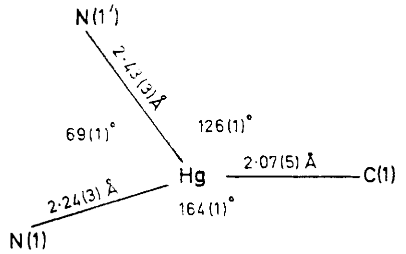

FIGURE 2 Stereochemistry of mercury in the cation

Approximately trigonal geometry for Hg^{II} in the compounds $[SMe_3][HgI_3]$ [28] and $HgTiO_3$ [29] can be satisfactorily accounted for by an sp^2 hybridization bonding model. However, for $[MeHg(bipy)][NO_3]$ the irregular co-ordination geometry is clearly inconsistent with sp^2 hybridization (Figure 2), and presumably reflects the strong tendency for linear geometry in organomercury(II) compounds and the low acceptor properties of linear organomercury compounds towards additional ligands.[1,12-17,30] A spectroscopic study of $[MeHg(bipy)][NO_3]$ and related three-co-ordinate $MeHg^{II}$ complexes is reported elsewhere.[31]

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