

Structural Studies of Steric Effects in Phosphine Complexes. Part 6. The Synthesis, Characterization and Molecular Structure of the Dinitrato-(trimesitylphosphine)mercury(II) Dimer

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The synthesis and crystal and molecular structure of the dinitrato(trimesitylphosphine)mercury(II) dimer is reported. The compound $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$ belongs to the monoclinic space group $P2_1/c$ (C_{2h}^2 , No. 14) with $a = 19.940(3)$, $b = 17.588(2)$, $c = 16.403(2)$ Å, $\beta = 100.36(1)^\circ$ and $Z = 4$; the asymmetric unit contains two independent half dimers. The structure was refined to a final R of 0.056 for 4220 observed reflections measured by diffractometer. The mercury coordination in both dimers I and II is characterized by three strong nearly coplanar bonds (in I Hg–P 2.395(3), Hg–O 2.180(12) and 2.419(9), and in II Hg–P 2.418(3), Hg–O 2.257(8), and 2.342(9)) and three weaker Hg–O bonds in the range 2.58–2.90 Å. Both independent trimesityl phosphine ligands have the same regular propeller conformation (Hg–P–C–C torsion angles 42 to 49°) and the largest C–P–C angles (mean value 113.2(5)°) and cone angle ($\theta = 208^\circ$) yet determined. The main difference between the two independent dimers is the orientation of the non-bridging nitrate groups. Nitrate vibrational and phosphine ^1H and ^{31}P n.m.r. data are also presented for $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$.

Introduction [1]

Recent studies [2] have clearly shown that the steric requirements of the substituents on phosphorus have a marked effect on the stereochemistry and the chemical reactivity of metal complexes of phosphorus ligands. In order to evaluate the role of steric effects in these complexes we have undertaken a study of metal complexes of tertiary phosphines containing bulky substituents. X-ray analysis [3] of complexes of tricyclohexylphosphine, tris(*t*-butyl)phosphine, and tri-*o*-tolylphosphine, showed that such bulky phosphines are better described as irregular conic cogs rather than as solid cones. The concept of a

'ligand profile' [3] was developed to provide maximum cone angle data and to allow precise comparison of the conformations of the groups bonded to phosphorus. As part of this systematic study, we report herein the preparation, characterization, and crystal and molecular structure determination of $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$ (mesityl = $\text{C}_6\text{H}_2(\text{CH}_3)_3$), the first complex of trimesitylphosphine to be characterized. Particular interest focuses on the conformation of the mesityl groups as Tolman [2] from molecular model studies has predicted the largest known cone angle ($\theta = 212^\circ$) for trimesitylphosphine.

Experimental

General Procedures

Microanalyses were performed by M-H-W Laboratories, Phoenix, Arizona. The melting point, conductance and infrared and Raman spectral measurements were made as reported previously [4]. ^1H and ^{31}P n.m.r. spectra were obtained on a Bruker WP-60 instrument operating in the FT mode. Trimesitylphosphine was prepared by a literature method [5].

Preparation and Characterization of Dinitrato(trimesitylphosphine)mercury(II)

A solution of trimesitylphosphine (1.00 mmol) in hot absolute ethanol (50 ml) was added to a suspension of $\text{Hg}(\text{NO}_3)_2$ (1.00 mmol) in ethanol (15 ml). The mixture was refluxed for 0.5 h, giving a clear solution, from which colourless crystals precipitated on cooling to room temperature. The product was washed with ethanol and ether and dried *in vacuo*; yield, 50%. For X-ray analysis, the product was recrystallized from dichloroethane. *Anal.* Found: C, 45.01; H, 4.75; N, 3.31; $\text{C}_{27}\text{H}_{33}\text{PN}_2\text{O}_6\text{Hg}$ requires C, 45.48; H, 4.66; N, 3.93; m.p. (decomp.) 168–170 °C.

The ^1H n.m.r. spectrum of the complex in CD_3OD solution showed singlets at 1.95 ppm, 2.38 ppm, and 2.59 ppm due to the three non-equivalent methyl groups and an unresolved multiplet (overlapping

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doublets?) centered at 7.18 ppm assigned to the aromatic protons. Restricted rotation of the mesityl groups is evident in the complex by the non-equivalence of the *ortho*-methyl groups. In $C_6D_5NO_2$ solution, the multiplets observed in the methyl and aromatic regions at ambient temperature resolved at 100 °C into two singlets (2.30 and 2.42 ppm in a ratio of 2:1 respectively) due to the methyl groups and two doublets (6.90 and 7.10 ppm) attributable to the aromatic protons. For the free phosphine, a $CDCl_3$ solution shows methyl resonances at 2.08 ppm and 2.27 ppm in a 2:1 ratio; the aromatic protons resonate at 6.83 ppm as a doublet. The ^{31}P n.m.r. spectrum of the complex in CH_3OH at ambient temperature shows a chemical shift at -1.81 ppm (δ , upfield from H_3PO_4 as reference), giving a coordination chemical shift of 37.2 ppm. The chemical shift of trimesitylphosphine (-39.0 ppm in C_6H_6) occurs at an anomalously high field, presumably for the same reason as postulated for tri-*o*-tolylphosphine [2, 6]. The coupling constant $^1J(^{199}Hg-^{31}P)$ of 10,278.3 Hz is the largest yet observed for a mercury-tertiary phosphine complex [7].

The vibrational spectrum of $HgP(mesityl)_3(NO_3)_2$ clearly shows the absence of ionic nitrate in the solid state and thus the slight conductance of the complex in nitromethane (Λ 7.45 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, $10^{-3} \text{mol dm}^{-3}$ solution) can be attributed to partial dissociation. Nitrate infrared spectral bands (in cm^{-1} , Halocarbon and Nujol mulls) occur at 1495(vs), 1450(vs), 1268(vs), 1250(vs), 990(vs), 811(m), 808(m, sh), 722(w, sh), 715(w, sh), and 706(w). Although ligand bands that occur at 1460, 1020, and 735 cm^{-1} interfere with a clear assignment of all the characteristic nitrate bands, the large number of bands is consistent with the presence of at least two types of coordinated nitrate groups. The observation of two Raman spectral bands at 1015 cm^{-1} and 1040 cm^{-1} assignable to the symmetric stretching mode of the nitrate group also supports this conclusion. Other Raman bands at 105 cm^{-1} and 163, 184 cm^{-1} might tentatively be assigned to $\nu(Hg-P)$ and $\nu(Hg-O)$ by analogy with previous assignments for $Hg(PR_3)(OAc)_2$ complexes [8].

Crystallographic Measurements

The crystals of the title compound were clear, colourless, elongated blocks with well-defined faces. Preliminary study of the crystals was carried out by Weissenberg and precession photography. The *a*-axis rotation picture showed very weak layer lines for *h* odd implying that the structure might contain two very similar molecules separated by *a*/2. On the basis of systematic absences (*h*0*l*, *l* odd; and 0*k*0, *k* odd) the crystals were uniquely assigned to space group $P2_1/c$ (C_{2h}^5 , No. 14). Unit cell dimensions $a = 19.940(3)$, $b = 17.588(2)$, $c = 16.403(2)$ Å, and $\beta = 100.36(1)^\circ$ were obtained from the least-squares

analysis of the setting angles of 12 reflections in the 2θ range $10-15^\circ$ which had been centred on a Hilger and Watts Y290 PDP8I controlled diffractometer using MoK_α radiation ($\lambda = 0.71069$ Å) monochromatized from a graphite crystal.

Intensity data were collected from a crystal of dimensions $0.32 \times 0.30 \times 0.26$ mm. mounted on an eucentric goniometer head with the *a* axis approximately parallel to the ϕ axis. The $\theta-2\theta$ scanning technique was used to collect a unique data set to a maximum θ of 20° . A symmetric scan range of 0.6° in 2θ was composed of 60 steps of 1 s duration. Background counts of 15 s were measured at the beginning and end of each scan with the counter stationary. Reflections for which the intensity of the diffracted beam exceeded 15,000 counts/s were automatically remeasured with aluminum foil attenuators inserted in order to be within the linear response range of the scintillation counter. The intensities of three standard reflections, measured at 100 reflection intervals, decreased by 42% during data collection; this was corrected for by appropriate scaling. The data were processed in a manner similar to that described previously [9]. A total of 5275 intensity maxima were collected of which 4220 reflections with $I > 2\sigma(I)$ were used throughout the solution and refinement of the structure. The data were corrected for Lorentz and polarization factors and for absorption ($\mu(MoK_\alpha) = 26.6 \text{ cm}^{-1}$) using Gaussian integration. Maximum and minimum values of transmission coefficients were 0.788 and 0.610, respectively.

All computations were carried out on the IBM 370/155 and Amdhal V5 computers at the University of Guelph. The program SHELX [10] was used for the structural analysis, Fourier synthesis, least-squares refinement and calculation of interatomic distances and angles. The program XANADU [11] was used for the calculation of torsion angles. The molecular plots and the stereoview of the unit cell were produced by ORTEP [12].

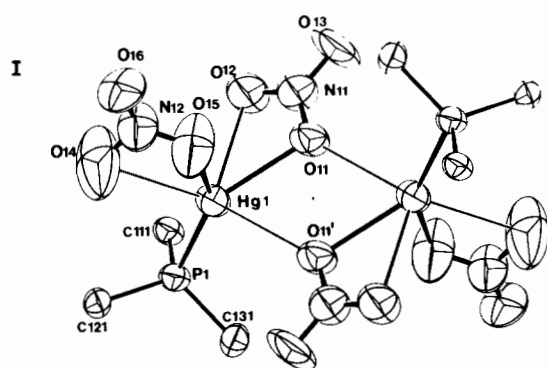
Structure Solution and Refinement

The structure was solved by the heavy-atom method. The mercury atoms were located from a sharpened three-dimensional Patterson synthesis; Fourier and subsequent difference Fourier maps revealed the positions of all the non-hydrogen atoms. The structure was refined by full-matrix least-squares techniques using the values of atomic scattering factors from International Tables for X-ray Crystallography, Vol. IV [13].

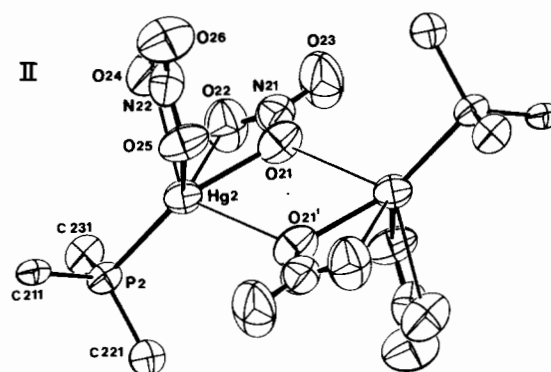
Three cycles of refinement with isotropic thermal parameters reduced the residual $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ to 0.127. Five more cycles of least-squares refinement in which all non-hydrogen atoms were allowed to vibrate anisotropically, reduced *R* to

TABLE I. Final Fractional Co-ordinates with Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Hg(1)	-24(1)	855(1)	1040(1)	N(21)	4434(6)	1202(6)	-584(7)
P(1)	-644(2)	694(2)	2151(2)	N(22)	6225(7)	1364(8)	807(6)
N(11)	1231(6)	128(7)	791(7)	O(21)	4838(4)	669(5)	-323(5)
N(12)	377(7)	2315(8)	312(8)	O(22)	4182(5)	1561(5)	-73(6)
O(11)	664(4)	46(5)	326(5)	O(23)	4274(8)	1329(6)	-1336(7)
O(12)	1248(5)	502(6)	1423(6)	O(24)	5773(5)	1844(6)	759(6)
O(13)	1739(5)	-182(7)	636(7)	O(25)	6112(4)	695(5)	1016(6)
O(14)	60(10)	2491(7)	894(10)	O(26)	6803(5)	1535(6)	673(6)
O(15)	278(7)	1637(7)	140(6)	C(211)	5105(6)	914(6)	3150(6)
C(16)	632(5)	2773(5)	-55(6)	C(212)	5031(6)	1447(7)	3759(7)
C(111)	13(5)	512(6)	3042(6)	C(213)	5596(7)	1699(7)	4312(7)
C(112)	584(7)	1013(7)	3186(7)	C(214)	6232(7)	1352(7)	4314(7)
C(113)	1163(7)	841(8)	3806(8)	C(215)	6284(6)	750(7)	3753(8)
C(114)	1146(7)	194(9)	4270(7)	C(216)	5724(6)	515(6)	3192(7)
C(115)	553(8)	-264(8)	4186(8)	C(217)	4347(7)	1820(8)	3882(8)
C(116)	-1(6)	-100(7)	3597(7)	C(218)	6874(7)	1643(8)	4932(8)
C(117)	615(7)	1750(7)	2733(8)	C(219)	5832(6)	-160(6)	2657(7)
C(118)	1797(8)	-29(11)	4900(10)	C(221)	4055(6)	-241(6)	2301(7)
C(119)	-618(8)	-609(7)	3591(8)	C(222)	3661(5)	-539(6)	1576(8)
C(121)	8926(5)	1599(6)	2229(6)	C(223)	3406(6)	-1279(7)	1563(7)
C(122)	8624(6)	1958(7)	1508(7)				
C(123)	8398(6)	2700(7)	1540(8)				
C(124)	-1565(6)	3097(7)	2277(10)	C(224)	3529(6)	-1720(6)	2297(9)
C(125)	-1290(6)	2715(6)	3020(7)	C(225)	3894(6)	-1435(7)	3045(8)
C(126)	-1080(5)	1960(7)	3013(7)	C(226)	4145(6)	-699(7)	3047(8)
C(127)	-1500(6)	1566(7)	650(7)	C(227)	3475(6)	-96(7)	782(6)
C(128)	-1799(7)	3932(7)	2308(9)	C(228)	3249(7)	-2549(6)	2278(10)
C(129)	-875(7)	1570(6)	3848(6)	C(229)	4489(6)	-404(7)	3925(7)
C(131)	-1214(6)	-113(6)	1871(6)	C(231)	3752(5)	1431(6)	2127(7)
C(132)	-1923(6)	-79(7)	1866(7)	C(232)	3916(6)	2165(6)	1850(7)
C(133)	-2335(6)	-651(7)	1502(8)	C(233)	3428(7)	2711(7)	1612(8)
C(134)	-2072(8)	-1282(8)	1144(8)	C(234)	2762(8)	2551(9)	1704(10)
C(135)	-1351(6)	-1353(7)	1198(7)	C(235)	2584(7)	1853(8)	2018(9)
C(136)	-928(6)	-759(6)	1557(7)	C(236)	3087(6)	1307(7)	2244(7)
C(137)	-2290(6)	540(7)	2282(9)	C(237)	4669(6)	2403(7)	1790(9)
C(138)	-2534(8)	-1932(9)	696(12)	C(238)	2189(9)	3167(10)	1451(13)
C(139)	-165(6)	-911(7)	1628(7)	C(239)	2827(7)	595(7)	2666(9)
Hg(2)	4947(1)	728(1)	1070(1)				
P(2)	4414(2)	702(2)	2281(2)				



(a)



(b)

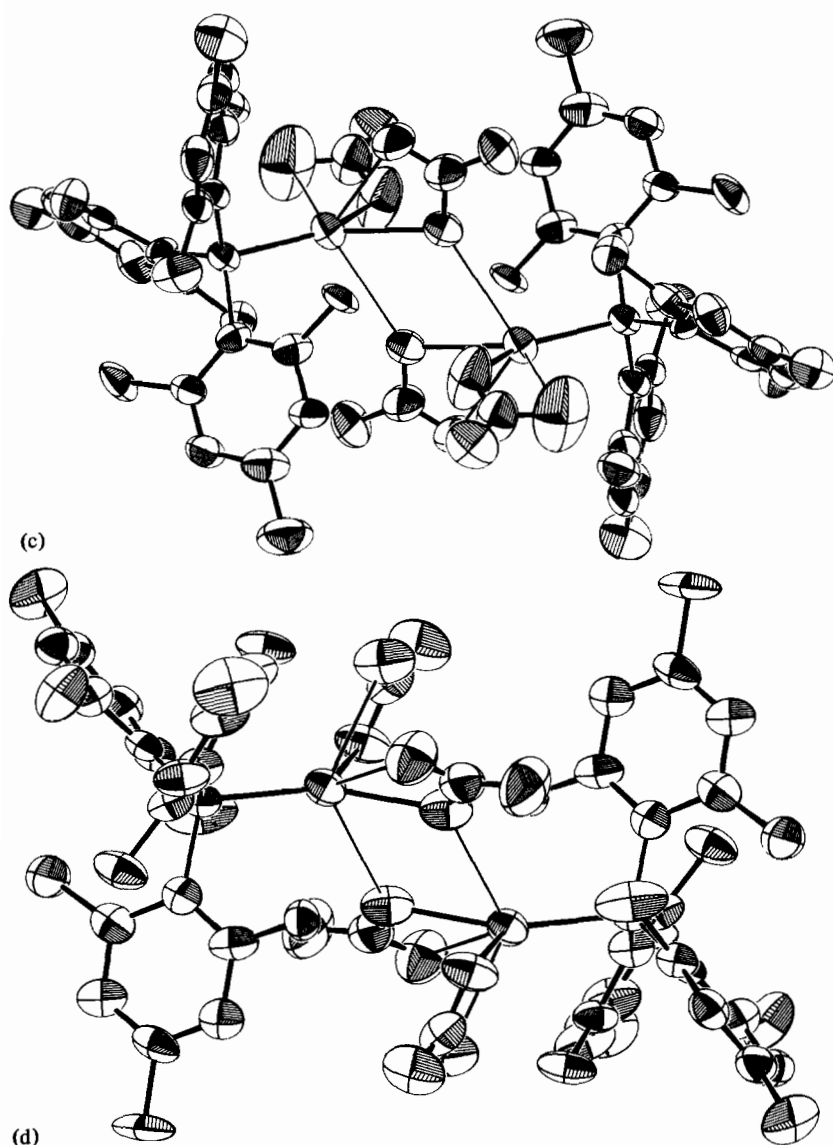


Fig. 1. Views with 50% probability ellipsoids of (a) and (c) dimer I, and (b) and (d) dimer II, of $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$ showing molecular geometry and details of our numbering schemes. For simplicity, only the mesityl carbons bonded to phosphorus are shown in (a) and (b).

0.056. During the final part of refinement, a weighting scheme of the form $w^{1/2} = 1/\Sigma\sigma^2(F) + 1.0 \times 10^{-3} F^2]^{1/2}$, was employed. The final weighted R_w ($\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$) was 0.065. A final difference synthesis showed five peaks which could be attributed to methyl protons but no other chemically significant information; no allowance was made for hydrogen atoms in the refinement. The final fractional coordinates with estimated standard deviations are given in Table I and selected molecular dimensions are in Table II. Details of anisotropic thermal parameters and a listing of the observed and calculated structure factors have been submitted to the editor and are available from the authors (ECA or GF).

The mercury coordination and our numbering scheme, are shown in Fig. 1 for both dimers; for simplicity only the mesityl carbons bonded to phosphorus are shown in Figs. 1a and 1b. The orientations of the mesityl groups may be seen in Fig. 1c and 1d, and also in Fig. 2 which shows the arrangement of six of the dimers in and around the unit cell outlines.

Discussion

The X-ray analysis of $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$ shows that the unit cell (Fig. 2) contains four dimeric molecules, half of each of the dimers I and II cor-

TABLE II. Interatomic Distances (Å) and Angles (°) for [HgP(mesityl)₃(NO₃)₂]₂.^a

a) Distances			
Hg(1)–P(1)	2.395(3)	Hg(2)–P(2)	2.418(3)
Hg(1)–O(11)	2.419(9)	Hg(2)–O(21)	2.257(8)
Hg(1)–O(12)	2.575(9)	Hg(2)–O(22)	2.637(10)
Hg(1)–O(14)	2.896(12)	Hg(2)–O(24)	2.670(11)
Hg(1)–O(15)	2.180(12)	Hg(2)–O(25)	2.342(9)
Hg(1)–O(11 ^I)	2.851(9)	Hg(2)–O(21 ^{II})	2.813(8)
N(11)–O(11)	1.25(1)	N(21)–O(21)	1.26(2)
N(11)–O(12)	1.22(2)	N(21)–O(22)	1.23(2)
N(11)–O(13)	1.22(2)	N(21)–O(23)	1.24(2)
N(12)–O(14)	1.27(2)	N(22)–O(24)	1.23(2)
N(12)–O(15)	1.23(2)	N(22)–O(25)	1.26(2)
N(12)–O(16)	1.18(2)	N(22)–O(26)	1.25(2)
P(1)–C(111)	1.81(1)	P(2)–C(211)	1.83(1)
P(1)–C(121)	1.82(1)	P(2)–C(221)	1.81(1)
P(1)–C(131)	1.83(1)	P(2)–C(231)	1.82(1)
b) Angles			
P(1)–Hg(1)–O(11)	135.5(2)	P(2)–Hg(2)–O(21)	148.7(2)
P(1)–Hg(1)–O(11 ^I)	108.2(2)	P(2)–Hg(2)–O(21 ^{II})	117.8(2)
P(1)–Hg(1)–O(12)	114.0(3)	P(2)–Hg(2)–O(22)	108.1(3)
P(1)–Hg(1)–O(14)	103.0(4)	P(2)–Hg(2)–O(24)	123.3(2)
P(1)–Hg(1)–O(15)	146.3(3)	P(2)–Hg(2)–O(25)	128.1(2)
O(11)–Hg(1)–O(11 ^I)	60.4(4)	O(21)–Hg(2)–O(21 ^{II})	60.9(4)
O(11)–Hg(1)–O(12)	50.0(3)	O(21)–Hg(2)–O(22)	50.8(3)
O(11)–Hg(1)–O(14)	119.9(4)	O(21)–Hg(2)–O(24)	77.9(3)
O(11)–Hg(1)–O(15)	78.1(4)	O(21)–Hg(2)–O(25)	82.9(3)
O(12)–Hg(1)–O(11 ^I)	109.8(4)	O(22)–Hg(2)–O(21 ^{II})	106.8(4)
O(12)–Hg(1)–O(14)	101.0(4)	O(22)–Hg(2)–O(24)	75.7(3)
O(12)–Hg(1)–O(15)	86.4(4)	O(22)–Hg(2)–O(25)	116.0(3)
O(14)–Hg(1)–O(11 ^I)	120.8(4)	O(24)–Hg(2)–O(21 ^{II})	114.3(4)
O(14)–Hg(1)–O(15)	44.7(5)	O(24)–Hg(2)–O(25)	50.3(3)
O(15)–Hg(1)–O(11 ^I)	87.6(4)	O(25)–Hg(2)–O(21 ^I)	74.5(4)
Hg(1)–P(1)–C(111)	103.8(4)	Hg(2)–P(2)–C(211)	104.7(4)
Hg(1)–P(1)–C(121)	105.4(4)	Hg(2)–P(2)–C(221)	105.4(4)
Hg(1)–P(1)–C(131)	106.5(4)	Hg(2)–P(2)–C(231)	106.6(4)
C(111)–P(1)–C(121)	112.3(4)	C(211)–P(2)–C(221)	114.7(5)
C(111)–P(1)–C(131)	113.1(5)	C(211)–P(2)–C(231)	112.9(5)
C(121)–P(1)–C(131)	114.7(5)	C(211)–P(2)–C(231)	111.6(5)
Hg(1)–O(11)–N(11)	99.6(7)	Hg(2)–O(21)–N(21)	104.5(8)
Hg(1)–O(12)–N(11)	92.8(7)	Hg(2)–O(22)–N(21)	86.9(8)
Hg(1)–O(14)–N(12)	82.2(8)	Hg(2)–O(24)–N(22)	87.2(8)
Hg(1)–O(15)–N(12)	120.6(10)	Hg(2)–O(25)–N(22)	102.3(8)
Hg(1)–O(11)–Hg(1 ^I)	119.6(2)	Hg(2)–O(21)–Hg(2 ^I)	119.1(2)
Hg(1)–O(11 ^I)–N(11 ^I)	140.3(7)	Hg(2)–O(21 ^{II})–N(21 ^I)	129.8(7)
O(11)–N(11)–O(12)	117(1)	O(21)–N(21)–O(22)	118(1)
O(11)–N(11)–O(13)	121(1)	O(21)–N(21)–O(23)	121(1)
O(12)–N(11)–O(13)	122(1)	O(22)–N(21)–O(23)	122(1)
O(14)–N(12)–O(15)	109(1)	O(24)–N(22)–O(25)	120(1)
O(14)–N(12)–O(16)	122(1)	O(24)–N(22)–O(26)	121(1)
O(15)–N(12)–O(16)	128(1)	O(25)–N(22)–O(26)	119(1)
c) Intermolecular Contacts			
O(16)···C(113 ^{III})	3.355	O(22)···C(217 ^{III})	3.370
O(16)···C(129 ^{III})	3.414	O(23)···C(217 ^{III})	3.275

(continued overleaf)

TABLE II. (continued)

O(22)···C(138 ^I)	3.326	• O(26)···C(127 ^{IV})	3.390
		O(26)···C(137 ^{IV})	3.403

^aThe superscripts on the second atom refer to the following transformations: I, $-x, -y, -z$; II, $1 - x, -y, -z$; III, $x, \frac{1}{2} - y, -\frac{1}{2} + z$; IV, $1 + x, y, z$.

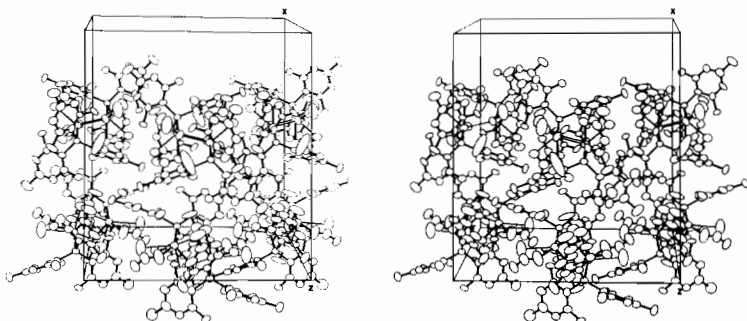


Fig. 2. Stereoview of the molecular packing diagram of $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$ showing six of the dimers.

responding to the asymmetric unit. Dimer I is centred on the inversion centre at (0, 0, 0) and dimer II at ($\frac{1}{2}$, 0, 0). The two dimers differ from each other in the configuration of the nitrate and trimesityl phosphine moieties at each mercury.

The mercury and phosphorus atoms are separated by 0.5 in x (but have similar y and z coordinates) and this accounts for the weak layer lines with h odd observed on the preliminary photographs.

In both dimers (Fig. 1) the mercury coordination is essentially trigonal planar with three strong bonds (Hg–P 2.395 in I and 2.418(3) Å in II, Hg–O 2.419 and 2.180 in I and 2.257 and 2.342 Å in II); similar geometry is found in $[\text{HgPCy}_3(\text{OAc})_2]_2$, and $[\text{HgP}(o\text{-tol})_3(\text{OAc})_2]_2$ [1]. Centrosymmetric dimer formation involves oxygen atoms O(11) in I and O(21) in II making longer contacts (2.85 and 2.81 Å respectively) with adjacent mercury atoms. In the isostructural $[\text{HgPCy}_3(\text{NO}_3)_2]_2$ [9] the Hg–O bridge distances were comparable (2.48 and 2.50(1) Å) presumably because of the less demanding steric requirements of the PCy_3 compared to the $\text{P}(\text{mesityl})_3$ ligand. Six-fold coordination at each mercury is completed by two further weak contacts involving the nitrate oxygen atoms (Hg–O 2.575–2.896 Å).

The N–O bond lengths in the nitrate groups are in the range 1.18(2)–1.27(2) Å with a mean value 1.24 Å. In dimer I the degree of asymmetry in the coordination of the terminal bidentate nitrate group is evident from the difference in the angle Hg(1)–O(13)–N(12) (120.6°) and Hg(1)–O(14)–N(12) (82.2°). The other unique nitrate group in dimer I and both unique nitrate groups of dimer II show less

asymmetry in both the Hg–O distances and the Hg–O–N angles (Table II).

The coordination about phosphorus is distorted tetrahedral in both dimers with Hg–P–C angles averaging 105.2 and $105.6(4)^\circ$ and C–P–C angles 113.3 and $113.1(5)^\circ$ in I and II respectively. In the free $\text{P}(\text{mesityl})_3$ [15] the C–P–C angles are 109.7° . In the sterically crowded $\text{HgP}(t\text{-Bu})_3(\text{OAc})_2$ [16], the Hg–P–C and C–P–C angles are 106.8 and $112.0(7)^\circ$ respectively. The extra distortion from tetrahedral (the largest yet observed in this direction) found in the mesityl dimers is a consequence of the greater overall steric bulk of the $\text{P}(\text{mesityl})_3$ ligand (see below). The Hg–P bond lengths (2.395 and 2.418(3) Å) are slightly longer than the corresponding distances in the $[\text{HgPCy}_3(\text{NO}_3)_2]_2$ (2.359(2) Å) [9], but are very close to the distances found in more crowded systems, e.g. $[\text{HgPCy}_3(\text{OAc})_2]_2$ (2.389(2) Å) [1], in $[\text{HgP}(o\text{-tolyl})_3\text{ClClO}_4]_2$ (2.396(4) Å) [14], and in $[\text{HgP}(o\text{-tolyl})_3(\text{OAc})_2]_2$ (2.415(4) Å) [1]. The mean bond lengths P–C (1.82(1) Å), aromatic C–C (1.40(2) Å) and $\text{CH}_3\text{--C}(\text{sp}^2)$ (1.55(2) Å) are in agreement with values found for the free phosphine [15].

Steric crowding in the bulky $\text{P}(\text{mesityl})_3$ moieties is relieved by out-of-plane displacements of phosphorus and methyl groups and by increases of (P)C–C–CH₃ angles. Thus, the phosphorus atoms are displaced by 0.11 to 0.36 Å from the mesityl ring plane and o -methyl groups 0.03 to 0.26 Å. The p -methyl groups also deviate from the ring planes but to a lesser extent 0.01 to 0.17 Å. At the o -methyl groups the mean $\text{CH}_3\text{--C}(\text{P})$ angle is 125° with a conco-

TABLE III. Deviations (A) from Least-squares Planes and Dihedral Angles within $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$.

Plane	Atoms in Plane	Equation	Greatest deviation of any atom from plane (A)
1	Hg(1), P(1), C(111)	$0.079x + 0.980y + 0.181z = 1.781$	0.00
2	C(111)–C(116)	$-0.390x + 0.561y + 0.731z = 4.179$	0.05
3	Hg(1), P(1), C(121)	$0.792x + 0.327y + 0.516z = 1.340$	0.00
4	C(121)–C(126)	$0.909x + 0.345y + -0.233z = -1.931$	0.04
5	Hg(1), P(1), C(131)	$0.711x - 0.616y + 0.338z = -0.379$	0.00
6	C(131)–C(136)	$0.098x - 0.462y + 0.881z = 2.981$	0.03
7	Hg(2), P(2), C(211)	$-0.199x + 0.977y - 0.074z = -0.677$	0.00
8	C(211)–C(216)	$0.223x + 0.677y - 0.701z = 0.916$	0.06
9	Hg(2), P(2), C(221)	$0.855x - 0.326y + 0.402z = 7.874$	0.00
10	C(221)–C(226)	$0.845x - 0.353y - 0.402z = 5.908$	0.02
11	Hg(2), P(2), C(231)	$0.655x + 0.680y + 0.328z = 7.223$	0.00
12	C(231)–C(236)	$0.191x + 0.367y + 0.910z = 4.328$	0.04

Dihedral angle between plane 1 and plane 2 = 49.4°
Dihedral angle between plane 3 and plane 4 = 44.6°
Dihedral angle between plane 5 and plane 6 = 49.2°
Dihedral angle between plane 7 and plane 8 = 48.0°
Dihedral angle between plane 9 and plane 10 = 47.5°
Dihedral angle between plane 11 and plane 12 = 47.7°

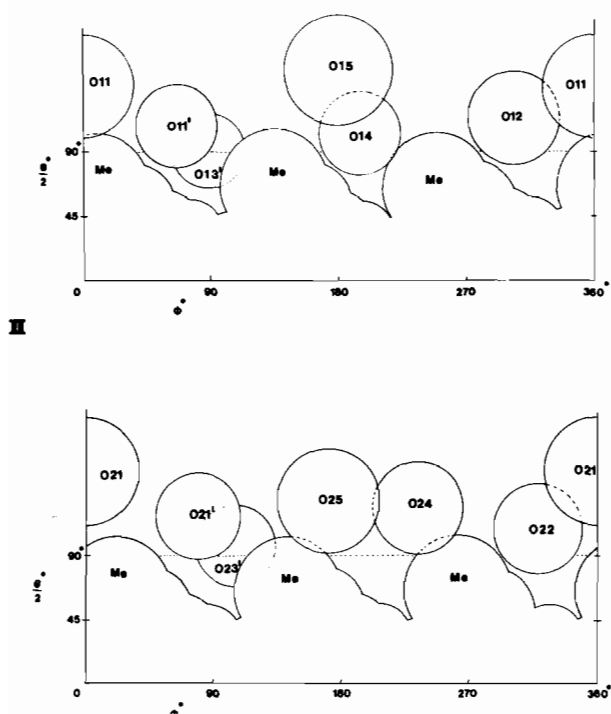


Fig. 3. Ligand profiles for $\text{P}(\text{mesityl})_3$ in dimers I and II of $[\text{HgP}(\text{mesityl})_3(\text{NO}_3)_2]_2$. The ordinate is the maximum semi-cone angle $\theta/2$, the abscissa is the angle ϕ through which a cone generating vector $\text{Hg} \rightarrow \text{X}$ is rotated about the $\text{Hg}-\text{P}$ bond. For full details see ref. 3. Also included in the profile diagrams are the outlines of the encroaching nitrate oxygen atoms.

mittant decrease in the $\text{CH}_3-\hat{\text{C}}-\text{C}(\text{C})$ angle (115°). At the *p*-methyl groups the mean $\text{CH}_3-\hat{\text{C}}-\text{C}$ angle is 120° . In each case, the *o*-methyl groups are displaced on the same side of the ring plane and the phosphorus and *p*-methyl groups to the other side.

To gauge the steric bulk of the $\text{P}(\text{mesityl})_3$ ligands we have prepared ligand profile diagrams (Fig. 3) and computed maximum semi-cone angles $\theta/2$ as described previously [3, 9, 16]. In dimer I maximum $\theta/2$ values are 102.7 , 103.1 and 106.4° with a mean value of 104.0° leading to a maximum cone angle θ of 208.0° . For dimer II equivalent $\theta/2$ values are 103.2 , 103.7 , and 104.2° and $\theta = 207.4^\circ$, in good agreement with the value 212° predicted by Tolman from molecular models [2]. Both $\text{P}(\text{mesityl})_3$ ligands adopt regular propeller conformations with dihedral angles between the appropriate $\text{Hg}-\text{P}-\text{C}$ and mesityl plane in the range $45-49(1)^\circ$, in the free ligand a value of 44° was found [15]. Also shown in Fig. 3 are the outlines of the nitrate oxygen atoms which are bonded to, or approach closely, the mercury atoms. In both dimers, the oxygen atoms of the bridging nitrate group (O(11), O(11^I), O(13^I) and O(21), O(21^{II}), O(23^{II})) 'fit' into the gaps between mesityl groups. It can readily be seen that the major difference between the two profiles is in the orientation of the terminal nitrate groups. In dimer I oxygens O(14) and O(15) also fit in the cog produced by the mesityl rings (allowing very different $\text{P}-\text{Hg}-\text{O}$ angles 103.0 and 146.3°) whereas in dimer II the corresponding oxygens (O(24) and O(25)) 'straddle'

two mesityl rings leading to P–Hg–O angles (123.3 and 128.1°) which are only slightly different.

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