# Synthesis of the Tridentate Pyridine Donor 2,6-Bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine (L), including Separation of *meso* and *rac* Diastereoisomers *via* Methylmercury(II) Derivatives, and an *X*-Ray Structural* Study of [HgMe(*meso*-L)]$NO_3$·$2H_2O$

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A synthesis of the new tridentate pyridine donor ligand 2,6-bis[1-phenyl-1-(pyridin-2-yl)-ethyl]pyridine, L, by reaction of 2,6-dichloropyridine with lithiated 2-(1-phenylethyl)pyridine is described. The ligand reacts with methylmercury(II) nitrate to form complexes of the *meso* and *rac* diastereoisomers of L, [HgMe(L)]$NO_3$·$2H_2O$, which may be readily separated by fractional crystallization. The ligands *meso*-L and *rac*-L may be liberated from the complexes by reaction with cyanide ion in water. The crystal structure of the *meso* complex has been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to $R = 0.046$ for 2 600 'observed' reflections [monoclinic, space group $P2_1/n$, with $a = 20.946(9)$, $b = 14.767(4)$, $c = 9.817(3)$ Å, $\beta = 91.12(2)°$, and $Z = 4$]. The [HgMe(*meso*-L)]$^+$ cations have irregular co-ordination geometry for the mercury atom '$HgCN_3$' with the ligand present as a tripodal tridentate. The central nitrogen forms the strongest bond to mercury [2.283(9)Å] with C–Hg–N 166.3(5)°, with the other nitrogen donors 2.546(11) and 2.595(10) Å from mercury and forming C–Hg–N angles of 113.3(5) and 113.7(5)°, respectively. $^1H$ N.m.r. spectra for the complexes suggest that the ligand is at least bidentate in methanol.

With polydentate nitrogen-donor ligands methylmercury(II) readily adopts co-ordination geometries higher than the characteristic linear geometry observed for unidentate ligands,[1] *e.g.* [HgMe($C_5H_5N$)]$NO_3$ ($C_5H_5N$ = pyridine) has Hg–N 2.12(2) Å and C–Hg–N 179.7(6)°,[2] but the corresponding bis(pyridin-2-yl)methane complex has Hg–N 2.16(1) and 2.75(2) Å,[3] compared with an estimated value of *ca.* 3.23 Å for the sum of mercury[4] and nitrogen[5] van der Waals radii. The higher co-ordination geometries are characterized by the presence of one stronger Hg–N interaction than the other(s), with the more strongly bound nitrogen forming the largest C–Hg–N angle, *e.g.* with bis(pyridin-2-yl)methane the shortest Hg–N bond forms an angle C–Hg–N 172(1)°, and the longest 106(1)°.[3]

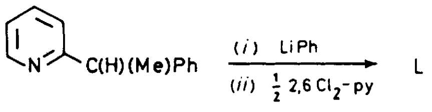
Although the complexes have irregular geometries for polydentates with pyridine, *N*-methylimidazole, or pyrazole donor groups, *e.g.* 'T-shaped' rather than trigonal for '$HgCN_2$' co-ordination in the bis(pyridin-2-yl)methane complex, two of the tridentate ligands studied have a much smaller range of Hg–N distances and more regular geometries than complexes of other tridentate ligands. Thus, the 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl ($Et_3$-terpy) complex has distorted square-planar geometry with Hg–N 2.26(2)—2.61(2) Å,[3] and the tris(pyridin-2-yl)methanol [$(py)_3COH$] complex has distorted tetrahedral geometry with Hg–N 2.28(1)–2.53(1) Å and C–Hg–N 119(1)—150(1)°.[6] As both of these complexes involve pyridine donor groups, we have sought further examples of this effect *via* synthesis of the new tridentate ligand 2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine, L.

The ligand L has two chiral centres, and molecular models suggest that the *meso* (*i.e.*, *R,S*) and *rac* (*R,R* and *S,S* enantiomers) diastereoisomers should both be able to act as planar tridentates (as for $Et_3$-terpy) or tripodal tridentates [as for $(py)_3COH$] towards methylmercury(II).

This paper reports the isolation of complexes of *meso* and *rac* forms of the ligand by reaction of L with $Hg^{II}Me$ nitrate, isolation of *meso*-L and *rac*-L from the $Hg^{II}Me$ complexes, and an *X*-ray structural analysis of [HgMe(*meso*-L)]$NO_3$·$2H_2O$. In the following paper, the synthesis of square-planar palladium(II) complexes of *meso*-L and *rac*-L are reported.[7]

## Results and Discussion

*Synthesis and Characterization of Ligands and Complexes.*—The tridentate ligand L was prepared by lithiation of 2-(1-phenylethyl)pyridine with phenyl-lithium followed by reaction with 2,6-dichloropyridine(2,6$Cl_2$-py) [equation (1)]. Methyl-



(1)

mercury(II) complexes were obtained from acetone solutions of methylmercury(II) nitrate and the ligand, with crystals of the *meso* complex forming within a few hours (44% yield after subsequent recrystallization), and crystals of the *rac* complex forming from the filtrate on slow vapour diffusion of diethyl ether into the acetone solution (13%).

The ligand is very insoluble in water, and thus the *meso* and *rac* diastereoisomers were readily isolated from their $Hg^{II}Me$

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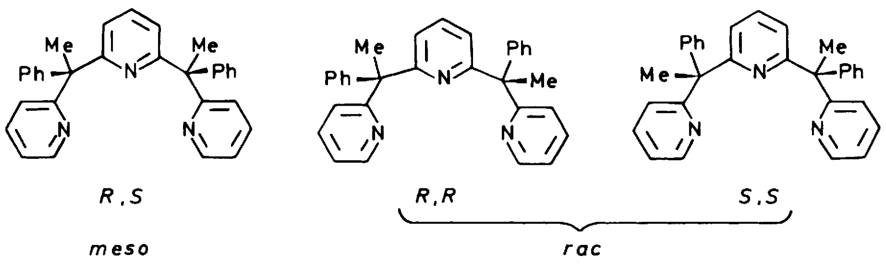
* *meso*-{2,6-Bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine-*N,N′,N″*}-methylmercury(II) nitrate dihydrate.

*Supplementary data available* (No. SUP 56587, 5 pp.): thermal parameters, H-atom parameters, mean planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

L



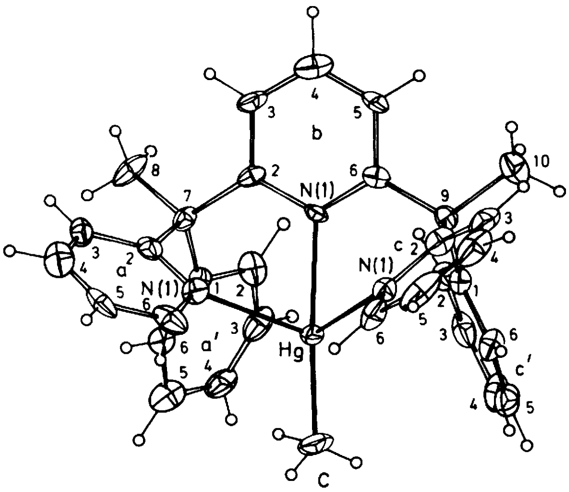


**Figure.** The cation $[HgMe(meso\text{-}L)]^+$. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, together with skeletal numbering

**Table 1.** Co-ordination geometry for the mercury atom and nitrate ion in $[HgMe(meso\text{-}L)]NO_3\cdot 2H_2O$; distances in Å, angles in °

| | | | |
|---|---|---|---|
| Hg–N(a1) | 2.546(11) | Hg–N(c1) | 2.595(10) |
| Hg–N(b1) | 2.283(9) | Hg–C | 2.048(15) |
| N(a1)–Hg–N(b1) | 76.0(3) | Hg–N(a1)–C(a2) | 118.4(8) |
| N(a1)–Hg–N(c1) | 88.8(3) | Hg–N(a1)–C(a6) | 122.5(9) |
| N(b1)–Hg–N(c1) | 75.3(3) | Hg–N(b1)–C(b2) | 118.3(7) |
| N(a1)–Hg–C | 113.3(5) | Hg–N(b1)–C(b6) | 120.2(8) |
| N(b1)–Hg–C | 166.3(5) | Hg–N(c1)–C(c2) | 115.5(7) |
| N(c1)–Hg–C | 113.7(5) | Hg–N(c1)–C(c6) | 123.0(9) |

Deviation of Hg from the '$C_5N$' mean planes of rings a, b, c: −0.46, 0.46, −0.25 Å

Nitrate ion: N–O(1,2,3) 1.06(3), 1.11(3), 1.16(3) Å; O(1)–N–O(2,3) 117(2), 121(2); O(2)–N–O(3) 120(2)°

complexes in high yield, 86 and 97% respectively, by formation of water soluble Hg(Me)CN [equation (2)]. Methylmercury(II) cyanide has log $K$ 14.1 in water,[8] considerably higher than that expected for the complexes, *e.g.* $[HgMe(terpy)]^+$ (terpy = 2,2′:6′,2″-terpyridyl) has log $K$ 6.35 in water.[9]

$$[HgMe(x\text{-}L)]^+ + CN^- \longrightarrow Hg(Me)CN + x\text{-}L \quad (2)$$
$$(x = meso \text{ or } rac)$$

The complexes and L have satisfactory microanalyses (C, H, Hg, or N) and $^1H$ n.m.r. spectra. Both complexes are hydrates, and as the *meso*-L complex is shown to be a dihydrate from crystallographic studies, the *rac*-L complex is formulated similarly in view of the unreliability of microanalytical results in the estimation of extent of hydration. The complexes exhibit identical $^1H$ n.m.r. spectra, but slightly different i.r. spectra in the region 1 100—500 cm$^{-1}$.

The diastereoisomers *meso*-L and *rac*-L have identical mass spectra to that of L, prepared by equation (1), but slightly different melting point, i.r. spectra in the region 900—500 cm$^{-1}$, and n.m.r. spectra. The *meso* diastereoisomer has m.p. 101—101.5, *rac*-L 98—99.5, L 96—97, and a *ca.* 1:1 mixture of *meso*-L and *rac*-L 95—96 °C. The *meso* and *rac* forms of L have slightly different $R_f$ values, with a mixture showing two maxima in a more extended spot (*meso*-L 0.8—0.68, *rac*-L 0.78—0.65, mixture 0.83—0.65, u.v. and iodine stain detection) after five developments on analytical silica gel plates with chloroform as solvent.

*Structure of* $[HgMe(meso\text{-}L)]NO_3\cdot 2H_2O$ *in the Solid State.*—Aspects of the geometry of $[HgMe(meso\text{-}L)]^+$ and the nitrate ion are given in Table 1, and the cation is shown in the Figure in an orientation allowing direct comparison with $[Pd(meso\text{-}L)(O_2CMe)]^+$ (Figure of ref. 7). Neighbouring cations are related by inversion centres, with atoms C(7) and C(9), in the Figure and ref. 7 (Figure), having chirality *S* and *R*, respectively. The nitrate ion is regular (within 2σ in bond lengths and angles) and unco-ordinated.

*meso*-L is present as a tripodal tridentate ligand, with N–Hg–N angles 76.0(3) (rings a,b), 88.8(3) (a,c), and 75.3(3)° (b,c). The central ring is more strongly bound to mercury, with Hg–N(b1) [2.283(9) Å] shorter than Hg–N(a1) [2.546(11) Å] and Hg–N(c1) [2.595(10) Å]. The mercury–nitrogen bond lengths differ by only 0.02—0.05 Å from those of both tripodal $(py)_3COH$ and $Et_3$-terpy, although the $Et_3$-terpy complex has the mercury atom well removed from the mean planes of the (outer) weakly co-ordinated rings (−0.886, −1.032 Å) compared with −0.46 (ring a) and −0.25 Å (ring c). The central nitrogen has C–Hg–N(b1) 166.3(5)°, a value intermediate between that for the $(py)_3COH$ [150(1)°] and $Et_3$-terpy complexes [171(1)°].

*Structure of the Complexes in Methanol.*—As the *meso* complex has two mercury–nitrogen interactions much weaker than the central pyridine interaction, it is possible that the complexes may have a different structure(s) in solution involving a lower co-ordination number(s), *e.g.* $Et_3$-terpy is tridentate in the solid state but bidentate in methanol.[3]

For pyridine and 14 substituted pyridines, including some with substituents in the 2- and 6- positions, *e.g.* 2,6-dimethylpyridine and the bulky -$CHPh_2$ group in α-phenyl-α-(pyridin-2-yl)toluene, the relationship $|^2J(^1H-^{199}Hg)| = -2.96 \log K_H + 241.6$ Hz has been established,[10] where log $K_H$ is the apparent protonation constant of the ligand determined in 50% dioxane–water. For polydentate pyridine donors, the coupling constant is higher than expected from this relationship if the ligand is co-ordinating as bidentate or tridentate.[3,6,11] For $[HgMe(meso\text{-}L)]^+$ and $[HgMe(rac\text{-}L)]^+$ the coupling constant is *ca.* 25 Hz greater than expected for unidentate binding, involving the same nitrogen as occurs on protonation, and thus the complex(es) in solution involve polydentate co-ordination.

The chemical shift of the $\mathrm{Hg^{II}Me}$ protons, −0.35 p.p.m., is further upfield than observed for any other complex ion $[\mathrm{HgMe(L)}]^+$, where L is a pyridine donor (0.70—1.16 p.p.m.),[3,6,11,12] consistent with the presence of two phenyl groups in orientations resulting in anisotropic shielding of the methyl protons, *e.g.* as observed on comparison of spectra for L = pyridine (1.08 p.p.m.) and 2-benzylpyridine (0.79 p.p.m.).[11]

*Discussion.*—The new tridentate ligand *meso*-L co-ordinates as a tripodal tridentate ligand to $\mathrm{Hg^{II}Me}$ and as a planar tridentate ligand to $\mathrm{Pd^{II}(O_2CMe)}$,[7] reflected most clearly in N(al)–M–N(c1) angles for the outer pyridine rings, 88.8(3) (M = Hg) and 177.8(2)° (M = Pd).[7] As the ligand is flexible in its co-ordination mode, it would appear that $\mathrm{Hg^{II}Me}$ prefers tripodal co-ordination. However, since palladium(II) has a strong preference for square-planar co-ordination, it is also possible that *meso*-L may be forced to adopt a less favoured conformation on binding to $\mathrm{Pd^{II}(O_2CMe)}$, while $\mathrm{Hg^{II}Me}$, which is more flexible in its co-ordination behaviour and forms only weak secondary interactions with the outer pyridine donor groups, may accommodate a conformation preferred by the ligand.

The flexibility in co-ordination behaviour of the *meso* form of the ligand, the synthesis of the diastereoisomer mixture (L) in moderate yield (*ca.* 30%) from 2-benzylpyridine, and the straightforward separation of *meso*-L and *rac*-L from their $\mathrm{Hg^{II}Me}$ complexes, indicate that the new ligand may be of value to studies in co-ordination chemistry generally, *e.g.* as a pyridine analogue of tridentate diethylenetriamine and as a relative of planar 2,2′:6′,2″-terpyridyl and tripodal tris(pyridin-2-yl)methane.

## Experimental

Microanalyses were by the Australian Microanalytical Service, i.r. spectra of complexes as Nujol and hexachlorobutadiene mulls (4 000—400 cm$^{-1}$) between KBr plates were measured with a Hitachi 270—30 spectrophotometer. $^1$H N.m.r. spectra in $\mathrm{CDCl_3}$ or $\mathrm{CD_3OD}$ were measured with a Bruker AM-300 spectrometer, mass spectra were obtained with a VG MM 70—70F spectrometer, and the protonation constants of the tridentate ligand (in 50% dioxane–water) were measured under the conditions described earlier,[10] using an automated equilibrium titrator with microcomputer implementations of MINIQUAD 75.[13]

Methylmercury(II) nitrate[14] and 2-(1-phenylethyl)pyridine[15] were prepared as described, 2,6-dichloropyridine was dried under vacuum over KOH, toluene and hexane were dried over $\mathrm{CaCl_2}$ followed by distillation from sodium and stored over sodium, bromobenzene was dried over $\mathrm{CaCl_2}$ followed by reflux and distillation over calcium turnings and storage over 4Å molecular sieves, dichloromethane was distilled, and diethyl ether was dried with a column of sieves followed by distillation over sodium–benzophenone and storage over sodium.

*Preparation of* 2,6-*Bis*[1-*phenyl*-1-(*pyridin*-2-*yl*)*ethyl*]*pyridine*, L.—A deep red solution was obtained on addition of 2-(1-phenylethyl)pyridine (2.604 g, 1.4 mmol) in diethyl ether (30 cm$^3$) to a solution of phenyl-lithium [from lithium (0.223 g, 3 mmol) and bromobenzene (1.64 cm$^3$, 1.6 mmol) in diethyl ether (30 cm$^3$)] under nitrogen. After stirring for 15 min 2,6-dichloropyridine (1.053 g, 0.71 mmol) in diethyl ether (50 cm$^3$) was added rapidly (dropwise), partly discharging the red colour with formation of a finely divided orange precipitate. Toluene (60 cm$^3$) was added and diethyl ether removed by distillation. The resulting suspension was refluxed for 20 h and, on cooling, the solution was hydrolysed with water (50 cm$^3$) and acidified with HCl(5 mol dm$^{-3}$). After isolation and extraction of the aqueous phase with dichloromethane (20 cm$^3$), the aqueous phase was neutralized with saturated $\mathrm{Na_2CO_3}$. Dichloromethane extracts (3 × 20 cm$^3$) were combined, dried over magnesium sulphate, filtered, and reduced in volume under vacuum to give a pale yellow viscous oil. On standing the oil crystallized, and the crystals were recrystallized from diethyl ether–hexane to give colourless needles (0.932 g, 32%), m.p. 96—97 °C (Found: C, 83.9; H, 6.3; N, 9.4. $\mathrm{C_{31}H_{27}N_3}$ requires C, 84.3; H, 6.2; N, 9.5%); $\nu_{\text{max.}}$ at 1 574s br, 1 494s, 1 470s, 1 444s, 1 428s, 1 152m, 1 026m, 992m br, 788m, 762m, 748s, 702s, 630m br, 594m, 550m cm$^{-1}$. Mass spectrum: *m*/*e* 441 (*M*, 35%), 426 (100), 260 (52), 259 (42), 183 (44), 182 (92), 181 (33), 180 (35), 168 (24), 167 (92), plus rings and their fragmentation ions. Potentiometric titration data were satisfactorily treated as arising from successive protonations of the ligand, with log $K_\mathrm{H}$ for the equilibria calculated as 3.87 and 2.28 for successive protonations.

*Synthesis of* $[\mathrm{HgMe(L)}]\mathrm{NO_3{\cdot}2H_2O}$ *Complexes.*—A filtered solution of the ligand (1.433 g, 3.2 mmol) in acetone (15 cm$^3$) was added to a filtered solution of methylmercury(II) nitrate (0.901 g, 3.2 mmol) in acetone (30 cm$^3$). The solution was allowed to evaporate in a draught at ambient temperature to a volume of *ca.* 20 cm$^3$ over a 2—3 h period, and colourless crystals of [HgMe(*meso*-L)]$\mathrm{NO_3{\cdot}2H_2O}$ were collected and air dried (1.352 g). The filtrate was transferred to a sealed chamber containing a beaker of diethyl ether, and on slow diffusion of ether vapour into the acetone solution two crops of [HgMe(*rac*-L)]$\mathrm{NO_3{\cdot}2H_2O}$ were obtained and combined (0.42 g, 13%). The *meso* complex was recrystallized by dissolution in warm acetone (60 cm$^3$) and evaporation to *ca.* 30 cm$^3$ to give colourless crystals (0.494 g). Further crops were obtained on continued volume reduction to give an overall yield of 1.087 g (44%).

[HgMe(*meso*-L)]$\mathrm{NO_3{\cdot}2H_2O}$. Found: C, 51.5; H, 4.6; Hg, 27.9. $\mathrm{C_{32}H_{34}HgN_4O_5}$ requires C, 50.9; H, 4.5; Hg, 26.7%. I.r. absorption: 3 570vw vbr, 3 468w vbr, 3 128vw, 3 058vw, 2 988w, 1 590m and 1 580m, 1 494w, 1 470m, 1 448m, 1 380vs and 1 330vs br and 1 292m as part of broad $\nu(\mathrm{NO_3^-})$, 1 190w, 1 157w, 1 137vw, 1 112vw, 1 070w, 1 050w, 1 025w, 1 013w and 1 004m, 912vw br, 890w, 841vw, 829w, 789w, 774m and 764s, 693s, 648w, 639w, 630m, 618m, 595w, 572m, and 566w cm$^{-1}$. $^1$H N.m.r.: 8.55 [m, 2 H, *J*(5,6) 5.26 Hz, H(6)(pyridines)], 8.12—8.07 (m, 1 H), 8.00—7.87 (m, 6 H), 7.51—7.46 (m, 2 H), 7.35—7.22 (m, 6 H), 6.84—6.80 (m, 4 H), −0.35 [s with coupling to $^{199}$Hg, 3 H, $^2J(^1\mathrm{H}\text{-}^{199}\mathrm{Hg})$ 256.6 Hz].

[HgMe(*rac*-L)]$\mathrm{NO_3{\cdot}2H_2O}$. Found: C, 51.8; H, 5.0; Hg, 27.4. $\mathrm{C_{32}H_{34}HgN_4O_5}$ requires C, 50.9; H, 4.5; Hg 26.7%. I.r. absorption: 3 550vw vbr, 3 456w vbr, 3 060w, 2 992w, 2 916w, 1 588m and 1 578m, 1 494w, 1 470m, 1 448m, 1 376vs br and 1 330vs br and 1 292m as part of broad $\nu(\mathrm{NO_3^-})$, 1 160w br, 1 137vw, 1 112vw, 1 068w br, 1 049vw br, 1 024vw, 1 011vw, 1 002w, 976w br, 868vw, 848vw br, 830vw, 788vw, 762m, 698m, 648w, 640vw, 630w, 616m, 594m, 574m, and 566m cm$^{-1}$. $^1$H N.m.r., as for *meso*-L complex.

*Isolation of* meso-L and rac-L *from the* $\mathrm{Hg^{II}Me}$ *Complexes.*—An identical procedure was used for both diastereoisomers, and the isolation of *meso*-L is given as an example. The $\mathrm{Hg^{II}Me}$ complex (0.088 g, 0.12 mmol) was suspended in water (15 cm$^3$) and sodium cyanide (0.0067 g, 0.14 mmol) was added with stirring. After stirring for 20 h the ligand was isolated by filtration using a fine sinter, washed with a large volume of water, dried in air, and then in a vacuum (0.0447 g, 0.1 mmol, 86%).

*meso*-L I.r. absorption: 3 064vw br, 2 984vw br, 1 586w and 1 571w, 1 496w, 1 470m, 1 446m, 1 430m, 1 370w br, 1 206vw br,

**Table 2.** Non-hydrogen atom co-ordinates for [HgMe(*meso*-L)]$NO_3 \cdot 2H_2O$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Hg | 0.181 23(3) | 0.154 17(4) | 0.385 53(5) |
| C | 0.183 6(8) | 0.039 7(10) | 0.503 4(16) |
| C(7) | 0.105 3(6) | 0.347 3(9) | 0.434 4(12) |
| C(8) | 0.056 4(7) | 0.423 8(9) | 0.457 3(17) |
| C(9) | 0.206 6(6) | 0.179 3(8) | 0.054 6(12) |
| C(10) | 0.199 9(8) | 0.176 0(12) | −0.105 5(15) |
| N(a1) | 0.209 9(5) | 0.297 5(7) | 0.517 5(11) |
| C(a2) | 0.164 0(6) | 0.362 1(8) | 0.532 0(12) |
| C(a3) | 0.169 6(7) | 0.433 0(9) | 0.620 3(13) |
| C(a4) | 0.223 7(8) | 0.438 9(11) | 0.694 9(16) |
| C(a5) | 0.272 2(7) | 0.376 7(11) | 0.685 4(12) |
| C(a6) | 0.263 0(7) | 0.304 1(11) | 0.597 4(14) |
| C(a′1) | 0.069 1(6) | 0.261 2(9) | 0.473 7(12) |
| C(a′2) | 0.029 2(7) | 0.220 1(11) | 0.373 9(14) |
| C(a′3) | −0.009 6(7) | 0.146 7(10) | 0.420 4(16) |
| C(a′4) | −0.005 7(7) | 0.114 9(9) | 0.544 9(17) |
| C(a′5) | 0.032 4(7) | 0.154 9(11) | 0.647 8(17) |
| C(a′6) | 0.069 7(6) | 0.228 1(9) | 0.601 2(13) |
| N(b1) | 0.155 5(4) | 0.268 6(6) | 0.237 9(8) |
| C(b2) | 0.128 6(5) | 0.346 5(9) | 0.289 9(12) |
| C(b3) | 0.124 6(7) | 0.422 0(8) | 0.203 3(14) |
| C(b4) | 0.148 9(7) | 0.419 2(10) | 0.075 7(17) |
| C(b5) | 0.172 0(7) | 0.342 0(10) | 0.025 8(12) |
| C(b6) | 0.175 2(6) | 0.265 9(8) | 0.110 9(12) |
| N(c1) | 0.282 8(5) | 0.177 2(7) | 0.242 4(10) |
| C(c2) | 0.272 8(6) | 0.180 3(8) | 0.103 5(14) |
| C(c3) | 0.325 6(8) | 0.183 6(9) | 0.022 4(16) |
| C(c4) | 0.386 3(8) | 0.182 5(11) | 0.079 3(20) |
| C(c5) | 0.396 1(7) | 0.182 8(10) | 0.209 3(21) |
| C(c6) | 0.341 6(7) | 0.177 7(9) | 0.296 8(15) |
| C(c′1) | 0.170 7(6) | 0.092 4(9) | 0.098 8(12) |
| C(c′2) | 0.104 6(7) | 0.088 2(10) | 0.105 6(14) |
| C(c′3) | 0.074 4(7) | 0.008 7(11) | 0.129 9(13) |
| C(c′4) | 0.108 6(8) | −0.069 8(10) | 0.159 1(16) |
| C(c′5) | 0.174 2(8) | −0.066 1(10) | 0.162 7(15) |
| C(c′6) | 0.205 0(7) | 0.013 3(9) | 0.129 5(14) |
| N | 0.403 4(8) | 0.137 7(12) | 0.650 6(24) |
| O(1) | 0.359 7(11) | 0.108 9(12) | 0.683 0(18) |
| O(2) | 0.446 5(11) | 0.093 8(18) | 0.654 4(30) |
| O(3) | 0.409 2(9) | 0.215 6(13) | 0.639 9(21) |
| O(W1) | 0.482 0(10) | −0.076 8(18) | 0.631 3(20) |
| O(W2) | 0.483 2(13) | −0.240 2(20) | 0.532 3(26) |

1 160w br, 1 080vw and 1 068vw, 1 026w, 990vw and 973w br, 866vw, 848vw, 786vw, 744w, 698w, 644vw, 630vw, 614vw, and 577w br $cm^{-1}$. $^1H$ N.m.r.: 8.55 [m, 2 H, *J*(5,6) 4.83 Hz, H(6)(pyridines)], 7.62 (m, 1 H), 7.52 (m, 2 H), 7.25—7.14 (m, including intense peaks at 7.22, 7.20, 7.16, 7.14, 10 H), 7.06 (m, 2 H), 7.0—6.92 (m, 4 H), and 2.16 (s, 6 H, $CH_3$).

*rac*-L I.r. absorption: 3 060vw br, 2 996w br, 1 585w and 1 569w, 1 496w, 1 470m, 1 446m, 1 430m, 1 372w br, 1 210vw br, 1 160w br, 1 080vw and 1 068vw, 1 026w, 992vw and 974w br, 847vw, 816vw, 793vw, 771w, 744w, 700w, 646vw and 632vw, and 551vw $cm^{-1}$. $^1H$ N.m.r.: 8.54 [m, 2 H, *J*(5,6) 4.82 Hz, H(6)(pyridines)], 7.54 (m, 2 H), 7.43 (m, 2 H), 7.24—7.16 (m, including intense peaks at 7.21, 7.19, 7.18, 6 H), 7.1—7.08 (m, 2 H), 7.05 (m, 2 H), 7.02—6.43 (m, 6 H), and 2.16 (s, 6 H, $CH_3$).

*Crystallography*.—A unique data set was measured within the limit $2\theta_{max.} = 50°$ at ~295 K using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode and using monochromatic Mo-$K_\alpha$ radiation ($\lambda = 0.710\ 6_9$ Å). 4 111 Independent reflections were measured, 2 600 with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block-diagonal least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ at convergence were $R = 0.046$; $R' = 0.047$ [$w = 1/\sigma^2(F)$ derived from $\sigma^2(I) = \sigma^2_{diff}(I) + 0.000\ 42\sigma^4_{diff}(I)$]. Neutral complex scattering factors were used;[16] computation used the XTAL 83 program system[17] implemented by S.R. Hall on a Perkin-Elmer 3240 computer. Atomic co-ordinates are given in Table 2.

*Crystal data*. $C_{32}H_{34}HgN_4O_5$, $M = 755.2$, monoclinic, space group $P2_1/n$ ($C_{2h}^5$, no.14), $a = 20.946(9)$, $b = 14.767(4)$, $c = 9.817(3)$ Å, $\beta = 91.12(2)°$, $U = 3\ 036(1)$ Å$^3$, $D_c(Z = 4) = 1.65$ g $cm^{-3}$, $F(000) = 1\ 496$, $\mu$(Mo-$K_\alpha$) = 49 $cm^{-1}$. Specimen: 0.10 × 0.35 × 0.09 mm; min. and max. transmission factors = 1.43, 1.79. $T$ ~295 K.

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