High Co-ordination Numbers for Methylmercury(II); *X*-Ray and ^{1}H N.M.R. Studies of [MeHgL]NO$_3$ (L = 4,4′,4″-Triethyl-2,2′:6′,2″-terpyridyl and Di-2-pyridylmethane)

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Summary Methylmercury(II) forms complexes [MeHgL]NO$_3$ (L = 2,2′:6′,2″-terpyridyls and di-2-pyridylmethane) where the ligands L are bidentate in methanol, but tridentate and bidentate, respectively, in the solid state with co-ordination geometries for mercury based on a near linear dominant C–Hg–N unit with additional weak Hg–N bonding.

METHYLMERCURY(II) is regarded as one of the simplest Lewis acids as its co-ordination geometry is restricted almost entirely to linear geometry.[1,2] As an essentially unifunctional cation it has been studied extensively as a prototype soft acid,[2,3] as a model spectroscopic probe for binding of metal ions to complex molecules,[4] and has also received attention owing to its role as a toxic species and its use in studies of polynucleotides[2,5] and proteins.[2] 2,2′-Bipyridyls act as bidentate ligands towards MeHg^{II} in [MeHgL]NO$_3$ to give three-co-ordinate mercury,[6,7] and we report here that 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et$_3$-terpy) acts as a tridentate ligand in the solid state but as a bidentate ligand in methanol, and that di-2-pyridylmethane (py$_2$CH$_2$) behaves as a bidentate ligand both in solution and in the solid state. These ligands were chosen for study as they can potentially act as unidentate ligands allowing MeHg^{II} to assume the commonly observed linear geometry, and because a ^{1}H n.m.r. method[6,8] showed promise for determination of co-ordination behaviour in solution for the complexes [MeHgL]NO$_3$.

The complexes were isolated as solids by reaction of MeHgNO$_3$ with the ligands in acetone, have satisfactory microanalyses (C, H, and Hg), and appropriate relative intensities in the ^{1}H n.m.r. spectra. *X*-Ray data were recorded with a Philips PW 1100 diffractometer using Mo-K_α radiation (λ = 0·7107 Å). General techniques employed have been described.[9]

Crystal data: [MeHg(Et$_3$terpy)]NO$_3$ (from ethanol): C$_{22}$H$_{26}$HgN$_4$O$_3$, M = 595·06, monoclinic, a = 9·115(2), b = 15·725(3), c = 15·566(3) Å, β = 94·465(14)°, U = 2224·34 Å^3, Z = 4, D_c = 1·776 g cm^{-3}, D_m = 1·77 g cm^{-3}, $F(000)$ = 1160, space group $P2_1/n$. A total of 6379 unique intensities ($2\theta_{max}$ = 60°) were recorded, giving 1438 observed intensities [$I \geqslant 3\sigma(I)$], and on refinement R = 0·067 and R^1 = 0·058.† [MeHg(py$_2$CH$_2$)]NO$_3$ (from methanol): C$_{12}$H$_{13}$HgN$_3$O$_3$, M = 447·84, monoclinic, a = 16·875(2),

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† All least-square refinements computed the agreement factors R and R^1 according to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R^1 = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/|\Sigma w^{\frac{1}{2}}|F_o|$ where F_o and F_c are the observed and calculated structure factors, respectively, and $w = 1/\sigma^2(F_o)$. The parameter minimized in all least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$.

b = 8·540(1), c = 9·353(1) Å, β = 96·544(8)°, U = 1339·10 Å^3, Z = 4, D_c = 2·221 g cm^{-3}, D_m = 2·22 g cm^{-3}, $F(000)$ = 840, space group $P2_1/n$. A total of 3885 unique intensities ($2\theta_{max}$ = 60°) were recorded giving 1142 observed intensities [$I \geqslant 3\sigma(I)$], and on refinement R = 0·054 and R^1 = 0·048.‡

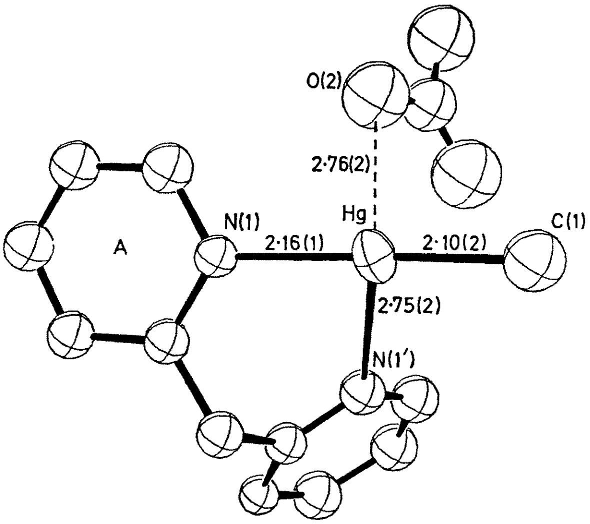

FIGURE 1. Perspective drawing of the molecular structure of [MeHg(py$_2$CH$_2$)]NO$_3$ showing numbering and bond lengths (Å). Important angles are: C(1)–Hg–N(1), 172(1), C(1)–Hg–N(1′), 106(1); and N(1)–Hg–N(1′), 78(1)°.

In both the py$_2$CH$_2$ and Et$_3$terpy complexes MeHg^{II} is strongly bonded to one nitrogen donor at 2·16(1) and 2·25(2) Å respectively, forming angles of 172(1) and 170(1)° with that nitrogen (Figures 1 and 2, ring A in both complexes). Additional Hg–N distances of 2·75(2) (py$_2$CH$_2$) and 2·52(2), 2·60(2) Å (Et$_3$terpy) are well within the sum of van der Waals radii,§ so that py$_2$CH$_2$ is present as a bidentate and Et$_3$terpy as a tridentate ligand. The CHgN$_2$ and CHgN$_3$ groups are approximately planar with the maximum deviations from mean planes being 0·080(1) (Hg) and −0·326(17) Å [N(1′)] in the Et$_3$terpy complex. The co-ordination geometry for the py$_2$CH$_2$ complex may be regarded as distorted 'T-shape', and for the Et$_3$terpy complex as highly distorted square planar. There is an additional Hg · · · O interaction to a nitrate ion in each complex, 2·76(2) and 2·79(2) Å, respectively. In both complexes Hg–N bond distances are longer than those in two-co-ordinate MeHg^{II} complexes of unidentate pyridines [2·10(2)—2·12(2) Å].[9,11,12]

For complexes of unidentate pyridines in methanol the coupling constant $J(^1\text{H}–^{199}\text{Hg})$ is in the range 224·0—229·6 Hz and follows the relation $J(^1\text{H}–^{199}\text{Hg})$ = − 2·83-

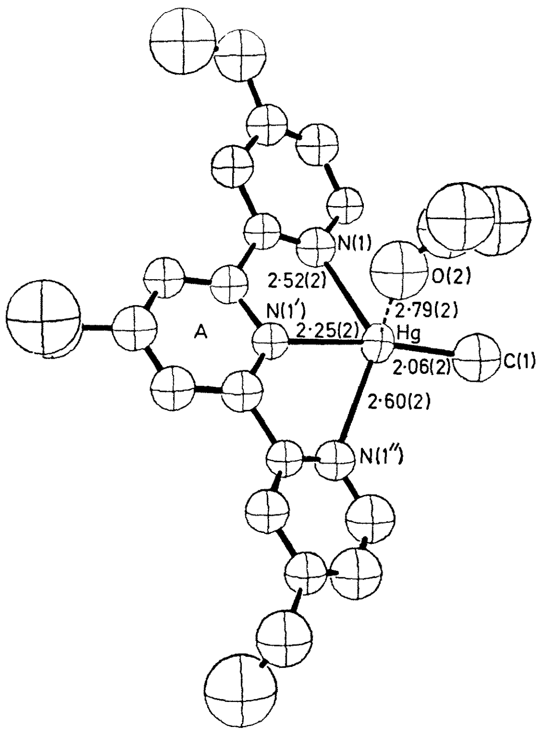

FIGURE 2. Perspective drawing of the molecular structure of [MeHg(Et$_3$terpy)]NO$_3$ showing numbering and bond lengths (Å). Important angles are: C(1)–Hg–N(1), 120(1); C(1)–Hg–N(1′), 170(1); C(1)–Hg–N(1″), 105(1); N(1)–Hg–N(1′), 70(1); and N(1′)–Hg–N(1″), 66(1)°.

pK_a + 240·9 Hz.[6,8] It is particularly significant that complexes of unidentate 3,3′-dimethyl-2,2′-bipyridyl (3,3′-dmbpy, 230·4 Hz) and 2-benzylpyridine (229·6 Hz), which has an α-substituent of identical steric bulk to 'CH$_2$py' in py$_2$CH$_2$, obey this relation, and also that the MeHg^{II} ^{1}H resonance for these two complexes is 0·2—0·4 p.p.m. upfield of all other py and bidentate bpy complexes. The upfield shift results from the presence of an unco-ordinated ring in an orientation close to the Me group such that it is shielded by the ring current anisotropy.[6,8,9,11] Complexes with bidentate bpy have $J(^1\text{H}–^{199}\text{Hg})$ 235·1—238·8 Hz, 4—15 Hz higher than py complexes, and, consistent with bidentate behaviour, [MeHg(py$_2$CH$_2$)]NO$_3$ has $J(^1\text{H}–^{199}\text{Hg})$ 235·4 Hz and the MeHg^{II} ^{1}H resonance is not shifted upfield. Complexes of terpy and Et$_3$terpy have $J(^1\text{H}–^{199}\text{Hg})$ 243 Hz indicating that they are not present as unidentate ligands, but the ^{1}H resonance is 0·36—0·44 p.p.m. upfield from the bpy complex and thus these ligands are present as bidentate ligands in methanol with one unco-ordinated ring.

The crystal structures and ^{1}H n.m.r. results presented here indicate that MeHg^{II} will accept high co-ordination

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ 3.0 Å [Hg 1·5 (ref. 10), N 1·5 Å (L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260)] or 3·23 Å using Grdenić's upper limit of 1·73 Å for the radius of mercury (see ref. 10). Recent structural determinations with close contacts between mercury atoms of 3·48(1)—3·51(1) Å (R. M. Barr, M. Goldstein, T. N. D. Harris, M. McPartlin, and A. J. Markwell, *J.C.S. Chem. Comm.*, 1974, 221) and 3·407(2)Å (A. J. Canty, M. Fyfe, and B. M. Gatehouse, *Inorg. Chem.*, 1978, **17**, 1467) lend support to the upper limit suggested by Grdenić.

numbers in both the solid state and solution with ligands that are potentially unidentate.

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[4] See, for example, G. Y. H. Chu, S. Mansy, R. E. Duncan, and R. S. Tobias, *J. Amer. Chem. Soc.*, 1978, **100**, 593, and references therein.

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