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Preliminary communication

THREE-COORDINATE MERCURY IN (2,2'-BIPYRIDYL)METHYLMERCURY(II) NITRATE AND RELATED COMPLEXES

ALLAN J. CANTY*, ANTHONY MARKER
Chemistry Department, University of Tasmania, Hobart, Tasmania 7001 (Australia)
and BRYAN M. GATEHOUSE
Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)
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Summary

Methylmercury(II) forms complexes $[MeHgL]^+ [NO_3]^-$ (L = bidentate ligand) having three-coordinate mercury; an X-ray crystal structure analysis shows that the complex with 2,2'-bipyridyl has a planar $CHgN_2$ group with unsymmetrically chelated 2,2'-bipyridyl.

Organomercury(II) cations, RHg^+, readily form linear two-coordinate complexes with neutral ligands [1]. The complex $[MeHg(2,2'\text{-bipy})]^+ [NO_3]^-$ having a potentially bidentate ligand has been isolated but its structure is unknown [2], although stability constant studies [3, 4] suggest that 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) are chelated to $MeHg^+$ in aqueous solution. In view of the novelty of three-coordination in organomercury chemistry we have studied complexes of this type by NMR spectroscopy and determined the crystal structure of the 2,2'-bipyridyl complex.

All of the complexes listed in Table 1 were isolated as white solids from addition reactions in acetone and have satisfactory microanalyses (C, H, Hg, N).

$$MeHgNO_3 + L \rightarrow [MeHgL]^+ [NO_3]^-$$

The mode of coordination of the bipyridyl ligands cannot be readily determined spectroscopically. However, except for the 3,3'-dmbipy complex, coupling constants $J(^1H—^{199}Hg)$ for the methylmercury group are similar in complexes of the bipyridyl and phenanthroline ligands (235.1-239.8 Hz), and are higher than in the pyridine and substituted pyridine complexes (227.5-229.6 Hz) (Table 1). An increase in coupling constant is observed on solvation of organomercury compounds by polar solvents [7], and thus an increase in coupling constant on replacing pyridine with potentially chelating bipyridyl and phenanthroline ligands probably indicates an increase in coordination number of mercury.

TABLE 1

^{1}H NMR PARAMETERS FOR THE METHYLMERCURY GROUP IN THE COMPLEXES [a]

Complex	δ(MeHg) [b]	$J(^1H-^{199}Hg)$ [c]
$MeHgNO_3$	2.597	251.8
$[MeHg(py)]NO_3$	2.564	229.6 (226.0 [d], 227 [e])
$[MeHg(2\text{-}mpy)]NO_3$ [f]	2.533	227.9
$[MeHg(3\text{-}mpy)]NO_3$	2.589	228.2
$[MeHg(4\text{-}mpy)]NO_3$	2.585	227.5
$[MeHg(bipy)]NO_3$	2.499	238.8
$[MeHg(6,6'\text{-}dmbipy)]NO_3 \cdot H_2O$ [g]	2.508	235.9
$[MeHg(5,5'\text{-}dmbipy)]NO_3$	2.518	237.1
$[MeHg(4,4'\text{-}dmbipy)]NO_3$	2.550	235.1
$[MeHg(3,3'\text{-}dmbipy)]NO_3$	2.893	230.4
$[MeHg(phen)]NO_3$	2.383	239.8
$[MeHg(2,9\text{-}dmphen)]NO_3 \cdot H_2O$ [h]	2.384	236.0

[a] 0.1M solutions in CD_3OD at 100 MHz. [b] Chemical shift upfield from internal 1,4-dioxane, accuracy to ca. ± 0.005 ppm. [c] Accuracy to ca. ± 0.5 Hz. [d] 0.2M in D_2O [5]. [e] 5 mole % in pyridine or D_2O [6]. [f] 2-mpy = 2-methylpyridine. [g] 6,6'-dmbipy = 6,6'-dimethyl-2,2'-bipyridyl. [h] 2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline. Other ligands similarly abbreviated.

Consistent with this interpretation, the ligand 3,3'-dmbipy, which cannot act as a chelate because of excessive steric interaction between the 3- and 3'-methyl groups in the *cis* conformation, forms a complex with a value of $J(^1H-^{199}Hg)$ (230.4 Hz) similar to the complexes of unidentate ligands as expected for the structure $[Me-Hg-N{\sim}N]^+$ in solution.

$[MeHg(2,2'\text{-bipyridyl})]^+ [NO_3]^-$ crystallizes from methanol with space group $P\bar{1}$, $a = 10.229(5)$, $b = 9.289(5)$, $c = 6.841(4)$ Å, $\alpha = 88.98(4)$, $\beta = 105.57(5)$, and $\gamma = 84.81(4)°$. Calculated ($Z = 2$) and observed densities are 2.31 and 2.39 g cm^{-3} respectively. The structure analysis was based on 1241 independent non-zero intensities (after rejection of 500 observed reflections having $I/\sigma(I) < 4$) collected by the ω scan technique out to 2θ(Mo-K_α) = 46° on a Philips PW1100 diffractometer. Solution of the structure was achieved by Patterson and Fourier methods. Block diagonal least squares refinement with anisotropic temperature factors for all atoms except hydrogen (with inclusion of hydrogen atom contributions in the structure factors in idealized positions with isotropic thermal parameters 1 Å^2 > the equivalent isotropic thermal parameter of the atom to which they are attached) converged to a conventional R factor of 0.058.

Aspects of the crystal and molecular structure are shown in Figs. 1 and 2. The coordination around mercury is planar and three-coordinate with 2,2'-bipyridyl unsymmetrically chelated. Both Hg—N distances are significantly less than the sum of Van der Waals radii, 3.0 Å (or 3.23 Å with an upper limit of 1.73 Å for the radius of mercury [8]) and are similar to Hg—N bond distances in other 2,2'-bipyridyl and 1,10-phenanthroline complexes of mercury, e.g. 2.373(9) and 2.399(8) Å in $[HgBr_2(bipy)]_2$ [9] and 2.42(2)-2.52(2) Å in $Hg(SCN)_2(phen)_2$ [10]. There are two nitrate oxygen atoms 2.990(57) and 2.993(38) Å from mercury, one above and one below the $[MeHg(bipy)]^+$ group (Fig. 1). There is no crystallographic evidence of nitrate coordination, the nitrate ion is regular (within one standard deviation in bond lengths and angles) and the Hg—O distances correspond closely to the sum of Van der Waals radii (2.9, or 3.13 Å upper limit).

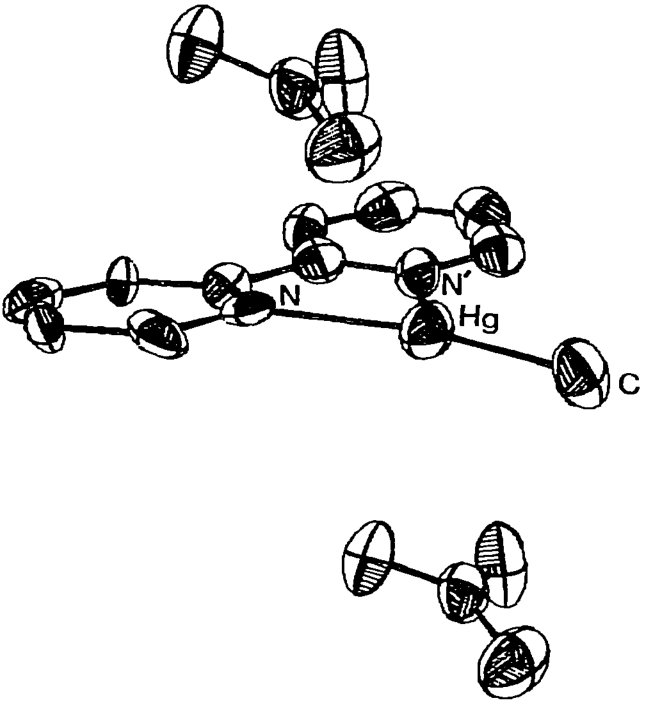

Fig. 1. Structure of $[MeHg(2,2'\text{-bipyridyl})]^+[NO_3]^-$ showing the positions of neighbouring nitrate ions.

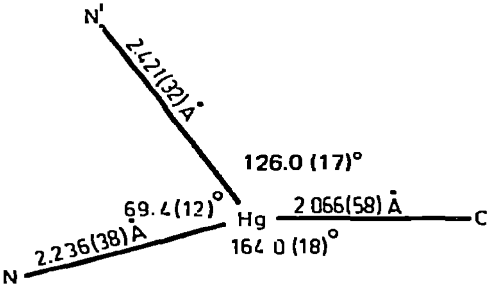

Fig. 2. Stereochemistry of mercury in the $[MeHg(2,2'\text{-bipyridyl})]^+$ cation.

The stereochemistry of mercury is planar but highly distorted from the trigonal geometry expected for sp^2 hybridized mercury, e.g. $[HgI_3]^-$ in $[Me_3S]^+$ $[HgI_3]^-$ [11]. The distortion presumably reflects the strong tendency for linear two-coordination in organomercury compounds [1, 8] with the shortest Hg—N bond forming the largest angle (164.0(18)°) with the methylmercury group.

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