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Organometallic Compounds Containing a Guanidinium Group. Phenylmercury(II) Derivatives of Creatine and Creatinine

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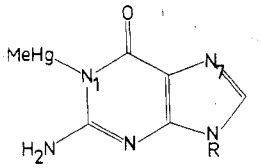
Phenylmercury(II) replaces a proton of creatine, $H_2NC^+(NH_2)NMeCH_2CO_2^-$, in basic solution to form the zwitterionic complex $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$. Creatine and creatinine ($C_4H_7N_3O$) react with $PhHg((OH)NO_3)_{1/2}$ in aqueous ethanol to form a 2:1 complex $[(PhHg)_2C_4H_6N_3O][NO_3]$ which exists in two crystalline forms. Creatinine forms a 1:1 complex $[PhHg(C_4H_7N_3O)][NO_3]\cdot{}^1/_2H_2O$ at pH 1.4 on reaction with $PhHg((OH)NO_3)_{1/2}$ in the presence of nitric acid.

The 1:1 and 2:1 complexes may be interconverted. Creatinine hydronitrate, $[H_2NCNMeCH_2CONH][NO_3]$, and the PhHg^{II} complexes of creatinine have similar infrared (including deuterated derivatives) and ^{1}H NMR spectra, consistent with retention of the creatinine ring and presence of a guanidinium group in the complexes. An X-ray structural analysis of one crystalline form of the 2:1 complex shows bonding of PhHg^{II} groups to the exocyclic and ring nitrogens of creatinine to form the cation $[PhHgNHCNMeCH_2CONHgPh]^+$. Crystal data: space group $P2_1/c$, $Z = 4$, $a = 13.389$ (6) Å, $b = 7.605$ (4) Å, $c = 17.924$ (8) Å, $\beta = 93.32°$, $R = 0.0639$ for 1226 reflections having $I \geq 4\sigma(I)$.

The coordination chemistry of guanidines has been little studied and for organomercury(II) cations is restricted to a MeHg^{II} derivative of guanosine 5′-phosphate (I)[2,3] which is



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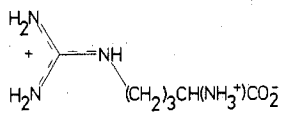

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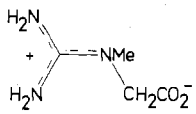

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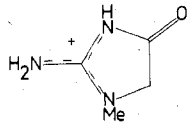

IV

formed at ca. neutral pH following loss of a proton from N(1).[3,4] Some other guanidines are more basic than guanosine and exist in the protonated guanidinium form in vivo, e.g., arginine (II) and creatine (III),[5] and are thus expected to form complexes with organometallic cations. Organometallic and metal ion derivatives of creatine and its metabolite creatinine, which may be protonated[6] to give IV, have not been described. We report here a study of the coordination chemistry of PhHg^{II} with creatine and creatinine.

Experimental Section

Creatine monohydrate and creatinine are commercially available and were used as received. Basic phenylmercuric nitrate (Hopkin and Williams) was recrystallized from ethanol. D_2O of isotopic purity 99.75% was obtained from the Australian Atomic Energy Commission. Deuterated ethanol (ca. 80% deuterated) was prepared by refluxing ethanol with an equal volume of D_2O for several hours ($CaCl_2$ guard tube), followed by distillation (82–84 °C). Recrystallization of creatine hydrate twice from D_2O gave the compound with >95% deuteration (IR estimation).

Microanalyses were by the Australian Microanalytical Service, Melbourne, and are given in Table I. Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls[7] were recorded with a Perkin-Elmer 577 spectrophotometer. ^{1}H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. The pHs of reaction solutions were measured with a Pye Unicam Model 290 Mk 2 pH meter.

Preparation of Complexes. In all syntheses solvent removal prior to recrystallization was by a rotary evaporator at ambient temperature.

$PhHgNHC^+(NH_2)NMeCH_2CO_2^-$. As this complex has very low solubility in water and ethanol, and thus preparation of the deuterated complex requires synthesis rather than recrystallization of the complex from deuterated solvent, sodium hydroxide used in syntheses was prepared from sodium ethoxide and water. Sodium ethoxide, prepared by dissolving sodium (0.032 g, 1.39 mmol) in dry ethanol (10 mL), was added to a solution of creatine hydrate (0.196 g, 1.31 mmol) in warm water (20 mL). Basic phenylmercuric nitrate (0.43 g, 1.36 mmol of PhHg^{II}) in ethanol (110 mL) was added, followed by removal of ca. 80 mL of solvent, giving a solution of pH 13.5. A white precipitate of the complex was collected (0.23 g, 43%) and, on standing overnight, the filtrate gave more product (0.05 g, 9%). The complex darkens above ca. 130 °C. The deuterated complex was prepared similarly using deuterated solvents.

Creatinine Complexes. $[PhHg(H_2creat)][NO_3]\cdot{}^1/_2H_2O$. Nitric acid (0.54 M, 1.4 mL) was added to a solution of basic phenylmercuric nitrate (0.264 g, 0.83 mmol) and creatinine (0.088 g, 0.78 mmol) in ethanol (55 mL)/water (10 mL). Removal of ca. 40 mL of solvent gave a solution of pH 1.4 and fine needles (0.15 g, 43%). The crystals undergo loss of volume at 110 °C, mp 168–169 °C dec. Drying under high vacuum at ambient temperature gave the anhydrous complex (Table I, absence of ν(OH) in IR spectra).

The complex, ca. 80% deuterated, crystallized as needles from a solution of 0.03 g of the hemihydrate dissolved in warm D_2O (2 mL) after filtration to remove a white residue. On exposure to air D_2O of crystallization exchanged rapidly with atmospheric water, IR absorptions of D_2O decreasing in intensity with appearance of absorptions of H_2O. A sample of $[PhHg(D_2creat)][NO_3]\cdot{}^1/_2H_2O$ in a desiccator with D_2O atmosphere gave $[PhHg(D_2creat)][NO_3]\cdot{}^1/_2D_2O$ after several days.

$[(PhHg)_2Hcreat][NO_3]$ (1). (a) From Creatine Hydrate. Basic phenylmercuric nitrate (0.484 g, 1.53 mmol) in ethanol (120 mL) was added to creatine hydrate (0.116 g, 0.78 mmol) in water (20 mL). Approximately 80 mL of solvent was removed and, after the mixture stood overnight in an open flask, colorless cubic crystals formed from a solution of pH 5.7. They were collected and dried in vacuo with phosphorus pentoxide (0.175 g, 31%); mp 175 °C dec.

(b) From Creatinine. Approximately 70 mL of solvent was removed from a solution of basic phenylmercuric nitrate (0.42 g, 1.32 mmol) and creatinine (0.078 g, 0.69 mmol) in ethanol (110 mL)/water (20 mL). After the mixture stood overnight, crystals of **1** formed (0.09 g, 19%, IR identification) from a solution of pH 6.7.

A sample of **1** ca. 80% deuterated was prepared from a solution of **1** (0.025 g) in 2 mL of 2:1 EtOD/D_2O in a small evaporating dish. The dish was protected from draughts with an inverted beaker, and the complex formed by slow crystallization overnight.

$[(PhHg)_2Hcreat][NO_3]$ (2). (a) From Creatine Hydrate. Basic phenylmercuric nitrate (0.465 g, 1.47 mmol) in ethanol (110 mL)

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Table I. Analytical Data for the Complexes

Complex	% calcd				% found			
	C	H	Hg	N	C	H	Hg	N
$PhHgNHC^+(NH_2)NMeCH_2CO_2^-$	29.45	3.21	49.19	10.30	29.76	3.31	49.10	10.33
$[H_3creat][NO_3]^a$	27.28	4.58		31.81	27.38	4.60		31.54
$[PhHg(H_2creat)]NO_3$	26.52	2.67	44.30	12.37	26.19	3.02	44.20	12.33
$[PhHg(H_2creat)]NO_3 \cdot {}^1/_2H_2O$	26.01	2.84	43.43	12.13	25.51	3.19	43.20	12.39
$[(PhHg)_2Hcreat]NO_3$ (1)	26.34	2.21	55.00	7.68	26.32	2.26	55.00	7.62
$[(PhHg)_2Hcreat]NO_3$ (2)	26.34	2.21	55.00	7.68	26.59	2.28	55.25	7.68

[a] $[H_3creat]^+ = [C_4H_8N_3O]^+$, protonated creatinine.

was added to creatine hydrate (0.101 g, 0.68 mmol) in water (20 mL). Approximately 85 mL of solvent was removed, and a small quantity of needlelike crystals formed within 1 h from a solution of pH 5.9. Clusters of needles were collected after the mixture stood overnight (0.19 g, 38%); mp 175–176 °C dec.

(b) From Creatinine. Approximately 110 mL of solvent was removed from a solution of basic phenylmercuric nitrate (0.72 g, 2.27 mmol) and creatinine (0.124 g, 1.10 mmol) in ethanol (150 mL)/water (20 mL). After the mixture was chilled at −10 °C, a white precipitate of **2** formed (0.23 g, 25%, IR identification) from a solution of pH 5.3.

The complex, ca. 80% deuterated, was prepared from a solution of basic phenylmercuric nitrate (0.119 g, 0.38 mmol) and creatine hydrate (0.029 g, 0.19 mmol) in EtOD (26 mL) and D_2O (4 mL). After 45 min ca. 20 mL of solvent was removed and a white precipitate collected (0.04 g, 29%).

Interconversions between $[(PhHg)_2Hcreat][NO_3]$ (1 and 2). Complex **1** (0.055 g) was dissolved in ethanol (2 mL)/water (1 mL) by warming the mixture briefly on a steam bath. Upon evaporation to dryness a residue of **2** was obtained. Complex **2** (0.15 g) was warmed with ethanol (6 mL)/water (3 mL), and the solution was filtered into a small conical flask. Ethanol (2 mL) was added and, after the mixture was chilled at −10 °C for 2 days, crystals of **1** formed (0.025 g) (IR identifications).

Interconversions between $[PhHg(H_2creat)][NO_3] \cdot {}^1/_2H_2O$ and $[(PhHg)_2creat][NO_3]$. Addition of nitric acid (0.54 M, 2 mL) to a mixture of $[(PhHg)_2Hcreat][NO_3]$ (**1** and **2**; 0.20 g, 0.27 mmol) in ethanol (3 mL) gave $[PhHg(H_2creat)][NO_3] \cdot {}^1/_2H_2O$ (0.02 g, 32%) from the chilled filtrate on filtration (pH 0.9). Gentle heating (60 °C) of a solution of $[PhHg(H_2creat)][NO_3] \cdot {}^1/_2H_2O$ (0.04 g) in water (1 mL) gave a precipitate of $[(PhHg)_2Hcreat][NO_3]$ (**1** and **2**), and from the filtrate, crystals of $[PhHg(H_2creat)][NO_3] \cdot {}^1/_2H_2O$ formed.

$[H_3creat][NO_3]$. Creatine hydrate (0.7 g, 4.69 mmol) was warmed with nitric acid (4 M, 2 mL) for 5 h on a steam bath. From the solution at −10 °C a white crystalline product was obtained, after which it was washed with ethanol (0.51 g, 62%); mp 167 °C. The deuterated compound crystallized from a solution of $[H_3creat][NO_3]$ in D_2O.

Crystallography

Crystals of $[(PhHg)_2Hcreat][NO_3]$ (**1**) isolated from ethanol/water (above) have formula $C_{16}H_{16}Hg_2N_4O_4$, mol wt 729.5, and are monoclinic with $a = 13.389$ (6) Å, $b = 7.605$ (3) Å, $c = 17.924$ (8) Å, $\beta = 93.32°$, $V = 1822.0$ Å^3, $D_{measd} = 2.64$ g cm^{-3}, $D_{calcd} = 2.66$ g cm^{-3}, $Z = 4$, $F(000) = 1327.9$, $\mu = 162.4$ cm^{-1} for Mo Kα radiation (λ 0.7107 Å), and space group $P2_1/c$ (No. 14, C_{2h}^5) from systematic absences $h0l$ (l odd) and $0k0$ (k odd). The standard Philips PW 1100 X-ray diffractometer computer program was used to determine the cell parameters.

Intensity data were collected from a very small single crystal, 0.075 × 0.063 × 0.03 mm, mounted on a silica capillary. A unique data set of 4694 reflections was collected out to 2θ(Mo Kα) = 56° using the ω-scan technique with a scan speed of 0.05° s^{-1}, a scan width of 0.90° and an allowance for dispersion. The 1226 reflections that obeyed the condition $I \geq 4\sigma(I)$ were used in the refinement, leaving 3468 reflections classified as unobserved. Three standard reflections were monitored every 1 h and showed no significant intensity variation.

The data were processed using a program written for the PW 1100 diffractometer, details of which have been commented upon elsewhere.[8] Values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects, but not for absorption or extinction owing to the smallness of the crystal and the lack of development of crystal faces. All calculations were performed on the Monash University B 6700 computer using program SHELX-76,[9] which includes correction for anomalous dispersion. The structure was solved by Patterson and Fourier techniques. Full-matrix least-squares refinement was used. Phenyl groups were refined as rigid groups (C–C = 1.395 Å, C–H = 1.08 Å, all angles 120°). Positions of hydrogen atoms were idealized; e.g., C(2)H(21)H(22) was refined as a methylene group and C(3)H(31)H(32)H(33) as a primitive methyl group, and all hydrogen atoms were given $U = 0.094$. Data were weighted in final cycles with $w = 1/\sigma^2(F)$; the final refinement involved 113 variables and gave $R = 0.0639$ [where $R = \sum||F_o| - |F_c||/\sum|F_o|$] and $R_w = 0.0605$ [where $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$]. For the 3468 unobserved reflections 57 had $3\sigma(I) \leq I \geq 4\sigma(I)$ and these had d between 2.01 and 4.09, where $d = ||F_o| - |F_c||/\sigma(F_o)$.

A table of observed and calculated structure amplitudes is available.[7] Positional and thermal parameters for all except hydrogen atoms bonded to carbon are presented in Tables II and III; data for hydrogens and least-squares plane data for the creatinine ring are available.[7] Molecular distances and angles are presented in Table IV.

Table II. Final Positional Parameters for All Atoms Except Hydrogens and Thermal Parameters for these Atoms Except for Mercury and Nitrate Oxygen Atoms in $[(PhHg)_2Hcreat][NO_3]$ (1)[a]

Atom	x	y	z	U, Å^2
Hg(1)	−800 (1)	6107 (2)	2114 (1)	
Hg(2)	−1159 (1)	2881 (2)	807 (1)	
N(1)	192 (2)	461 (3)	115 (1)	29 (6)
N(2)	30 (2)	339 (4)	85 (2)	54 (8)
N(3)	64 (2)	548 (4)	187 (1)	31 (7)
N(4)[b]	4 (3)	383 (5)	415 (2)	71 (9)
O(1)	142 (2)	740 (3)	263 (1)	50 (6)
O(2)[b]	72 (3)	291 (5)	440 (2)	
O(3)[b]	−80 (3)	375 (5)	435 (2)	
O(4)[b]	12 (2)	461 (4)	353 (1)	
C(1)	145 (3)	639 (5)	209 (2)	60 (9)
C(2)	235 (2)	590 (4)	175 (2)	35 (8)
C(3)	252 (3)	366 (5)	60 (2)	60 (9)
C(4)	92 (2)	447 (4)	124 (2)	32 (8)
C(5)	−224 (1)	683 (2)	224 (1)	48 (8)
C(6)	−280 (1)	604 (2)	278 (1)	38 (8)
C(7)	−382 (1)	644 (2)	281 (1)	46 (8)
C(8)	−427 (1)	763 (2)	230 (1)	59 (9)
C(9)	−370 (1)	841 (2)	176 (1)	50 (9)
C(10)	−269 (1)	801 (2)	173 (1)	67 (9)
C(11)	−265 (2)	256 (3)	60 (1)	50 (8)
C(12)	−334 (2)	346 (3)	101 (1)	61 (9)
C(13)	−435 (2)	340 (3)	79 (1)	64 (9)
C(14)	−468 (2)	246 (3)	16 (1)	80 (10)
C(15)	−399 (2)	156 (3)	−26 (1)	65 (9)
C(16)	−297 (2)	162 (3)	−4 (1)	49 (9)

[a] The Hg(1) and Hg(2) parameters are ×10^4; all others and U are ×10^3. Estimated standard deviations are given in parentheses. [b] Nitrate group.

Results and Discussion

Phenylmercury(II) salts are acidic (PhHgOH has $K_{dis} = 10^{-10}$ mol L^{-1} in water[10]) and thus "basic" phenylmercuric nitrate hydrolyzes according to

$$PhHg((OH)NO_3)_{1/2} + {}^1/_2H_2O \rightleftharpoons PhHgOH + {}^1/_2HNO_3 \quad (1)$$

In order to avoid cyclization of creatine to creatinine which occurs readily in acidic solution[11] and to encourage loss of a guanidinium proton, syntheses were initially attempted in basic solution.

Table III. Anisotropic Thermal Parameters for Mercury and Nitrate Oxygen Atoms in $[(PhHg)_2Hcreat][NO_3]$ (1)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	37 (1)	36 (1)	39 (1)	−3 (1)	8 (1)	4 (1)
Hg(2)	42 (1)	47 (1)	36 (1)	−3 (1)	4 (1)	−1 (1)
O(2)	120 (11)	139 (12)	64 (11)	32 (11)	32 (11)	16 (11)
O(3)	138 (11)	134 (12)	93 (11)	1 (1)	90 (10)	−13 (11)
O(4)	69 (10)	84 (11)	47 (10)	11 (10)	−16 (10)	35 (10)

[a] All values are $\times 10^3$ with estimated standard deviations in parentheses. Anisotropic parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}b^*c^*kl + \ldots)]$.

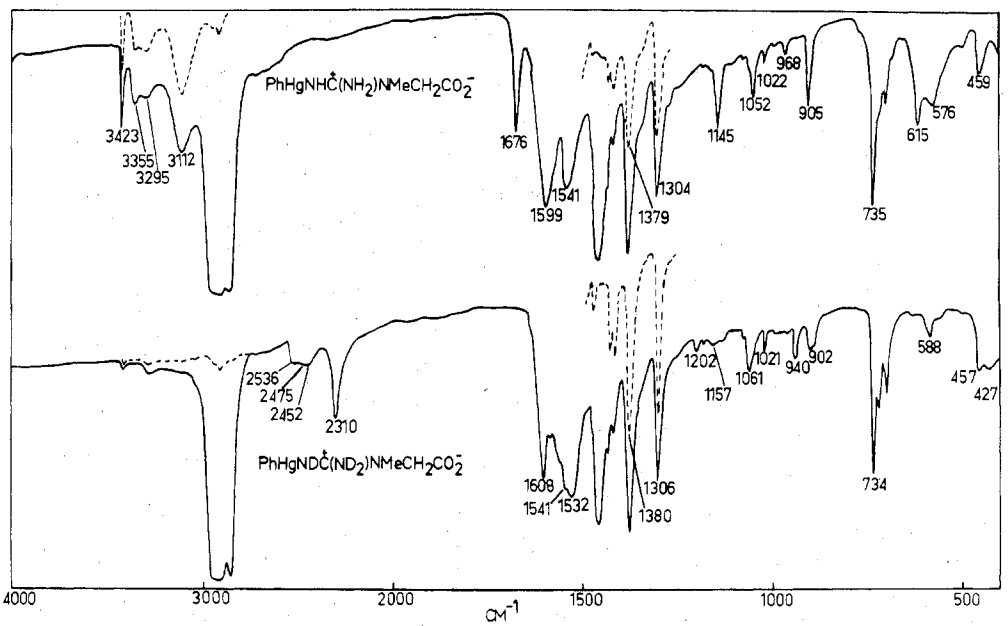
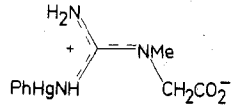


Figure 1. Infrared spectra of $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$ and $PhHgNDC^+(ND_2)NMeCH_2CO_2^-$ as Nujol (—) and hexachlorobutadiene (- - -) mulls.

Reaction of equimolar amounts of $PhHg^{II}$, creatine hydrate, and sodium hydroxide in aqueous ethanol resulted in precipitation of a 1:1 complex from a solution of pH 13.5.

$$PhHg^+ + (H_2N)_2C^+NMeCH_2CO_2^- + OH^- \rightarrow PhHg(C_4H_8O_2N_3) + H_2O \quad (2)$$

Physical and spectroscopic properties are consistent with the zwitterionic structure V related to crystalline creatine hydrate



V

(III),[12] rather than carboxylate coordination as in $HN{=}C(NH_2)NMeCH_2CO_2HgPh$. The latter complex would be expected to hydrolyze in aqueous solution to give a guanidinium group and OH^-, but aqueous ethanol solutions of V are nonconducting (molar conductivity 4.6; KCl 76.2 ohm^{-1} mol^{-1} cm^2). Comparison of IR spectra of the complex and its deuterated analogue (Figure 1, Table V) allows assignment of $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$. The difference between these values, 162 cm^{-1}, is as expected for an ionic carboxylate, e.g., NaO_2CMe (164 cm^{-1}),[13,14] unidentate[15] acetate in $PhHgO_2CMe$ (221 cm^{-1}), and extensively hydrogen-bonded[12] carboxylate in creatine hydrate (196 cm^{-1}).

In the absence of base, reaction of $PhHg^{II}$ with creatine hydrate in aqueous ethanol in the mole ratio 2:1 gave *creatinine* complexes **1** and **2** which have analyses appropriate for $[(PhHg)_2Hcreat][NO_3]$ (Table I). Complex **1** was obtained when conditions of slow crystallization were used, and **2** precipitated as a powder by rapid solvent removal to low volume or as needles by chilling a concentrated solution. Complexes **1** and **2** may be interconverted by crystallization. Both **1** and **2** may be obtained from creatinine

$$2PhHg^+ + H_2creat \rightarrow H^+ + [(PhHg)_2Hcreat]^+ (1, 2) \quad (3)$$

and in syntheses from creatine reaction is assumed to proceed

Table IV. Molecular Distances (Å) and Angles (deg) for $[(PhHg)_2Hcreat][NO_3]$ (1), with Estimated Standard Deviations in Parentheses

For Hg(1), Hg(2), C(5), and C(11)			
Hg(1)–C(5)	2.03 (2)	Hg(2)–C(11)	2.02 (2)
Hg(1)–N(3)	2.06 (3)	Hg(2)–N(2)	2.00 (3)
C(5)–Hg(1)–N(3)	174 (1)	C(11)–Hg(2)–N(2)	170 (1)
Hg(1)–C(5)–C(6)	121 (1)	Hg(2)–C(11)–C(12)	121 (1)
Hg(1)–C(5)–C(10)	119 (1)	Hg(2)–C(11)–C(16)	118 (c)
For the Creatinine Ring			
C(1)–C(2)	1.43 (5)	C(3)–N(1)	1.50 (4)
C(1)–O(1)	1.23 (4)	C(4)–N(1)	1.36 (4)
C(1)–N(3)	1.32 (4)	C(4)–N(2)	1.33 (4)
C(2)–N(1)	1.54 (4)	C(4)–N(3)	1.43 (4)
C(2)–C(1)–N(3)	116 (4)	C(3)–N(1)–C(4)	128 (3)
C(2)–C(1)–O(1)	124 (4)	C(4)–N(2)–H(2)	105 (8)
N(3)–C(1)–O(1)	119 (4)	H(2)–N(2)–Hg(2)	119 (8)
C(1)–C(2)–N(1)	99 (3)	C(4)–N(2)–Hg(2)	135 (3)
N(1)–C(4)–N(2)	124 (3)	C(1)–N(3)–C(4)	105 (3)
N(1)–C(4)–N(3)	110 (3)	C(1)–N(3)–Hg(1)	126 (3)
N(2)–C(4)–N(3)	125 (3)	C(4)–N(3)–Hg(1)	125 (2)
C(2)–N(1)–C(3)	124 (3)		
For the Nitrate Ion			
N(4)–O(2)	1.21 (4)	N(4)–O(4)	1.27 (4)
N(4)–O(3)	1.21 (4)		
O(2)–N(4)–O(3)	123 (5)	O(3)–N(4)–O(4)	114 (4)
O(2)–N(4)–O(4)	120 (4)		

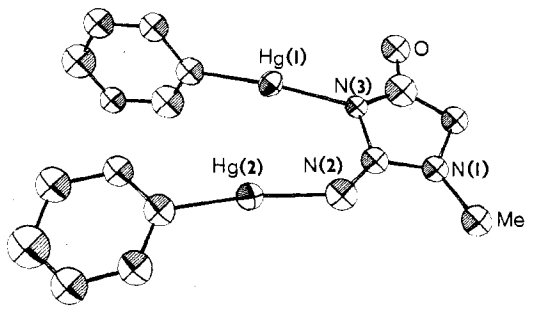


Figure 2. Structure of the cation $[(PhHg)_2Hcreat]^+$ in $[(PhHg)_2Hcreat][NO_3]$ (**1**). Hydrogen atoms are omitted.

Table V. Assignment of Carboxylate Absorptions and Absorptions of $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$ Shifted on Deuteration (cm^{-1})[a]

$PhHgNHC^+$-(NH_2)NMe-$CH_2CO_2^-$	$PhHgNDC^+$-(ND_2)NMe-$CH_2CO_2^-$	ν_D/ν_H	Assignment[b]
3423 m	2536 vw, b	0.74	$\nu(NH_x)$
3355 w	2475 vw, b	0.74	$\nu(NH_x)$
3295 w, b	2452 vw, b	0.74	$\nu(NH_x)$
3112 m, vb	2310 w	0.74	$\nu(NH_x)$
1676 m	1608 m	0.96	"ν(CN)" [c]
1599 s	1532 s	0.96	"ν(CN)" [c]
	1202 vw	0.75	NH_2 bend[c]
1541 s	1541 s, sh		$\nu_{as}(CO_2^-)$[c,d]
1379 vs	1380 vs		$\nu_s(CO_2^-)$[c,d]
1348 w, sh	1061 w	0.79	NH_x def
1145 m	940 vw	0.82	NH_x def
615 m	427 m	0.69	

[a] A simple diatomic oscillator approximation for R–X (X = H, D) gives expected values of ν_D/ν_H of 0.73 for ν(N–H) and ν(O–H)[16] and 0.976 for ν(C–NX_2). For –R–X bending modes $\nu_D/\nu_H \approx 0.7$.[16] [b] Similar assignments have been made for guanidinium chloride, $[C(NH_2)_3][Cl]$,[17] e.g.: "ν(CN)", a complex mode of the whole group, 1670 and 1640 shifted to 1587 cm^{-1} on deuteration; NH_2 bend 1538, ND_2 1137 (0.74); NH_2 rock (in plane) 1120, ND_2 928 (0.83); NH_2 twist 830, ND_2 620? (0.75); NH_2 wag ~520, ND_2 <400 (<0.77); CN_3 angle deformation (in plane) 525, $[C(ND_2)_3][Cl]$ 452 cm^{-1} (0.86).[17] [c] Creatine hydrate has "ν(CN)" 1693, ca. 1612 (vs, b) shifted to 1626 (s, sh) (0.96) and 1556 (m, sh) (0.97), respectively; NH_2 bend ca. 1612 (vs, b), ND_2 1156 (m) (0.72); $\nu_{as}(CO_2^-$, deuterated) ca. 1592 (vs); $\nu_s(CO_2^-)$ 1396 (s); NH_2 deformation 1125 (m, sh), 1113 (m), ND_2 897 (w) (0.80), 878 (m) (0.79) cm^{-1}. [d] Sodium acetate[13,14] $\nu_{as}(CO_2^-)$ 1578 (vs), $\nu_s(CO_2^-)$ 1414 (s) cm^{-1}. $PhHgO_2CMe$ $\nu_{as}(CO_2^-)$ 1591 (s), $\nu_s(CO_2^-)$ 1370 (s) cm^{-1}.

via cyclization of creatine to creatinine assisted by H^+[11] from hydrolysis of $PhHg((OH)NO_3)_{1/2}$ (eq 1; in reactions from both creatine and creatinine the pH of reaction solutions at crystallization was found to be within the range 5.3–6.7).

Reaction of $PhHg^{II}$, creatinine, and nitric acid in mole ratio 1:1:1 in aqueous ethanol gave crystals of $[PhHg(H_2creat)][NO_3]\cdot{}^1/_2H_2O$ from a solution of pH 1.4 on volume reduction

$$PhHg^+ + H_2creat \xrightarrow{H^+} [PhHg(H_2creat)]^+ \quad (4)$$

The 1:1 complex is also formed by acidification of solutions

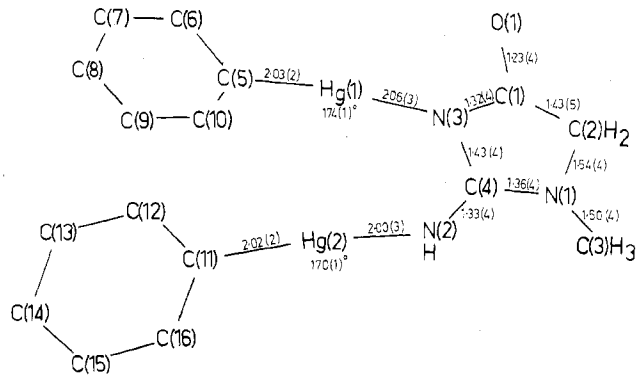


Figure 3. Selected structural parameters in the cation $[(PhHg)_2Hcreat]^+$.

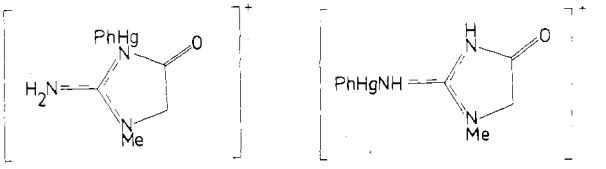
of **1** and **2** (pH 0.9), and dissolution of the solid 1:1 complex in water results in partial conversion to **1** and **2**.

$$[(PhHg)_2Hcreat]^+ (\mathbf{1}, \mathbf{2}) \underset{H_2O}{\overset{H^+}{\rightleftharpoons}} [PhHg(H_2creat)]^+ + PhHg^+ \quad (5)$$

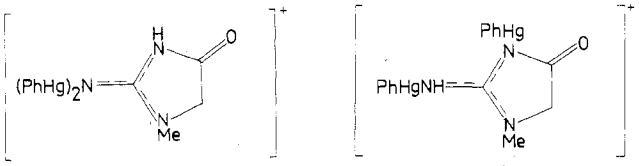
The compound $[H_3creat][NO_3]$ was prepared to assist with interpretation of ^1H NMR and IR spectra of the complexes.

$$H_2creat + HNO_3 \rightarrow [H_3creat][NO_3] \quad (6)$$

^1H NMR spectra of the complexes and $[H_3creat][NO_3]$ are very similar (Table VI) indicating that the complexes are based on a "creatinine" nucleus with a guanidinium group. Two structures are possible for the 1:1 complex (VI or VII), and



VI VII



VIII IX (1)

complex **2** may have structure VIII or be a different crystalline form of **1**, for which an X-ray crystallographic study has shown structure IX (Figures 2 and 3).

Complex **1** has $PhHg^{II}$ groups bonded to both exocyclic and ring nitrogens, N(2) and N(3), respectively. Mercury–carbon bond lengths, 2.02 (2) and 2.03 (2) Å, are similar to those found in other $PhHg^{II}$ complexes, e.g.: $PhHg(S\text{-}2,6\text{-}Me_2Ph)$, 1.97 (6) Å;[18] PhHgCN, 2.094 (16) Å;[19] Ph_2Hg, 2.085 (7) Å.[20] The mercury–nitrogen bond lengths, 2.00 (3) and 2.06 (3) Å, are similar to those found in linear Hg(II) complexes, e.g.:

Table VI. ^{1}NMR Data[a]

Compd	Ph	Me	CH_2	NH_x[b]
Creatinine (H_2creat)		−0.65 s (3)	0.11 s (2)	3.84 b (1.5)
$[H_3creat][NO_3]$		−0.51 s (3)	0.66 s (2)	5.42 b (2.3)
$[PhHg(H_2creat)][NO_3]\cdot{}^1/_2H_2O$	4.03–3.68 vb (5)	−0.48 s (3)	0.65 s (2)	5.2 vb (1.7)
$[(PhHg)_2Hcreat][NO_3]$ (**1**)	3.92–3.57 vb (10)	−0.44 s (3)	0.65 s (2)	5.3 vb (<1)
$[(PhHg)_2Hcreat][NO_3]$ (**2**)	3.9–3.6 vb (10)	−0.44 s (3)	0.65 s (2)	

[a] In Me_2SO-d_6 with Me_4Si as external lock and 1,4-dioxane as internal reference; shifts upfield of 1,4-dioxane are taken as negative. Integration values are given in parentheses. Creatine and $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$ are insoluble in Me_2SO-d_6. [b] Exchange with solvent and small quantities of water is assumed to account for low intensity or absence (**2**) of these resonances.

$(-Hg-NH_2-)_n^{n+}(Br^-)_n$, 2.07 Å;[21] Hg(1-methylthymine)$_2$, 2.04 Å.[22] Mercury atoms Hg(1) and Hg(2) are 3.407 (2) Å apart, close to the longer value in metallic mercury where mercury has six neighbors at 3.000 Å and six others at 3.466 Å.[23,24] Grdenić has suggested that the longer value defines an upper limit for the van der Waals radius of mercury,[24] i.e., 1.732 Å, and thus Hg(1)···Hg(2) = 3.407 (2) Å represents a van der Waals contact. The nitrate ion is not coordinated as it is regular (within one standard deviation in bond lengths and angles) and both Hg(1)···nitrate oxygen contacts (2.98 (3), 3.05 (3), 3.06 (3) Å) and Hg(2)···nitrate oxygen contacts (2.87 (3), 2.96 (3), 3.06 (3) Å) correspond closely to the sum of van der Waals radii, 2.9 (Hg 1.5,[24] O 1.4[25]) or 3.132 Å, using an upper limit of 1.732 Å for the radius of mercury.[24]

The creatinine ring is planar, with the largest deviation from the least-squares plane being 0.0374 Å [C(1)].[7] Mercury atoms Hg(1) and Hg(2) are 0.2914 and 0.05 Å from the plane. Bond lengths within the creatinine ring indicate delocalization of the carbonyl C(1)O with the guanidinium moiety as the C(1)–N(3) bond distance, 1.33 (5) Å, is appropriate for multiple-bond character.

Assignment of structures for $[PhHg(H_2creat)][NO_3]\cdot {}^1/_2H_2O$ and **2** is uncertain, but comparison of IR spectra of the complexes and their deuterated analogues (Table IX[7]) suggests that the 1:1 complex has the $PhHg^{II}$ group attached to the exocyclic nitrogen (VII) and that **2** has the same molecular structure as **1** (IX). All of the creatinine derivatives have two "ν(CN)" absorptions, with one of these very broad for $[H_3creat][NO_3]$ and **2** and split into a doublet for the 1:1 complex and **1**. Complexes **1** and **2** have very similar spectra; e.g., **1** has an NH deformation mode at 1176 cm^{-1} shifted to 1007 cm^{-1} on deuteration (ν_D/ν_H = 0.86), and **2** has an absorption at 1179 cm^{-1} shifted in the same manner. However, this absorption of **2** cannot be definitely attributed to an NH deformation of an exocyclic PhHgNH– group (IX) as $[H_3creat][NO_3]$ has similar absorption. Only $[H_3creat][NO_3]$ has an absorption attributable to an NH_2 bending mode, consistent with structure VII for the 1:1 complex, structure IX for complex **2**, and the crystal structure analysis of **1** (IX).

Facile complex formation by creatinine and $PhHg^{II}$, even in acid solution, suggests that molecules containing guanidine groups which are weakly (e.g., creatinine[6]) or strongly basic (e.g., creatine, arginine) may bind strongly with organometallic cations.

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Registry No. $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$, 66224-88-2; $[PhHg(H_2creat)][NO_3]$, 66225-07-8; $[(PhHg)_2Hcreat][NO_3]$, 66225-09-0; $[H_3creat][NO_3]$, 66224-89-3; $PhHgNDC^+(ND_2)NMeCH_2CO_2^-$, 66224-90-6; $[PhHg(D_2creat)][NO_3]$, 66271-17-8; $[(PhHg)_2Dcreat][NO_3]$, 66225-11-4.

Supplementary Material Available: Listings of IR spectra for $PhHgNHC^+(NH_2)NMeCH_2CO_2^-$, $[H_3creat][NO_3]$, $[PhHg(H_2creat)][NO_3\cdot {}^1/_2H_2O$, and $[(PhHg)_2Hcreat][NO_3]$ (**1**, **2**), a table of observed and calculated structure factor amplitudes, Table VII giving calculated positional and thermal parameters for hydrogen atoms, Table VIII showing the least-squares plane for the creatinine ring in $[(PhHg)_2Hcreat][NO_3]$ (**1**), Table IX giving ν(CO), "ν(CN)", and absorptions of creatinine derivatives shifted on deuteration, and Figures 4–7 showing infrared spectra of $[H_3creat][NO_3]$, $[PhHg(H_2creat)][NO_3\cdot {}^1/_2H_2O$, $[(PhHg)_2Hcreat][NO_3]$ (**1**, **2**), and their deuterated analogues presented in a manner similar to Figure 1 (16 pages). Ordering information is given on any current masthead page.

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