Methylation of Lead(II) and Methyllead(IV) Compounds in Water by a *Trans-*dimethylcobalt(III) Complex

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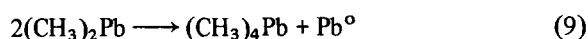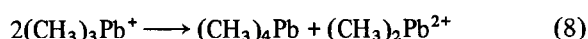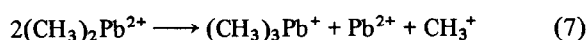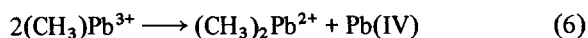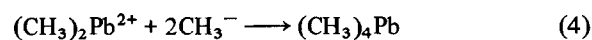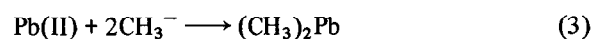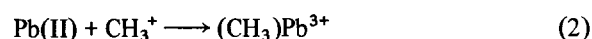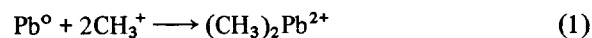*University of New Hampshire, Chemistry Department, Parsons Hall, Durham, N.H. 03824, U.S.A.*

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A factorial experiment determined separate and combined effects of $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ (I) (a methylcobalamin model and carbanion donor), CH_3I (a carbocation donor) and MnO_2 (an oxidizing agent) on the methylation of Pb^{2+} in aqueous systems. $(CH_3)_4Pb$ occurred only in the presence of (I). Methylation of $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ by (I) under similar conditions, produced high yields of $(CH_3)_4Pb$. Deuterium labelled (I) demonstrated the mechanism of CH_3^- transfer to both methyllead(IV) electrophiles.

Introduction

Several reports in recent years are concerned with environmental methylation of lead [1–4]. Interest in this process derives from increased toxicity of methyllead compounds, compared to their inorganic counterparts [5]. *In vitro* experiments with biologically active sediments failed to produce conclusive evidence about the ubiquity of the process [6–9]. However methylation studies in aqueous abiotic under model environmental conditions have provided important information about the possible mechanism of such a process in the natural environment [10–13].

Formation of methyllead compounds may proceed via the initial attachment of a methyl group to lead-(0), lead(II), or lead(IV) compounds with subsequent methyl groups originating from the same methyl donor or from dismutation of the original methyllead species. In eqns. 1–5 and 7 CH_3^+ and CH_3^- denote, respectively, carbocation and carbanion donors.

$$Pb^\circ + 2CH_3^+ \longrightarrow (CH_3)_2Pb^{2+} \qquad (1)$$

$$Pb(II) + CH_3^+ \longrightarrow (CH_3)Pb^{3+} \qquad (2)$$

$$Pb(II) + 2CH_3^- \longrightarrow (CH_3)_2Pb \qquad (3)$$

$$(CH_3)_2Pb^{2+} + 2CH_3^- \longrightarrow (CH_3)_4Pb \qquad (4)$$

$$(CH_3)_3Pb^+ + CH_3^- \longrightarrow (CH_3)_4Pb \qquad (5)$$

$$2(CH_3)Pb^{3+} \longrightarrow (CH_3)_2Pb^{2+} + Pb(IV) \qquad (6)$$

$$2(CH_3)_2Pb^{2+} \longrightarrow (CH_3)_3Pb^+ + Pb^{2+} + CH_3^+ \qquad (7)$$

$$2(CH_3)_3Pb^+ \longrightarrow (CH_3)_4Pb + (CH_3)_2Pb^{2+} \qquad (8)$$

$$2(CH_3)_2Pb \longrightarrow (CH_3)_4Pb + Pb^\circ \qquad (9)$$

Mono- and dimethyllead(II) (eqn. 3) species have not been isolated although they are probably intermediates in the formation of $(CH_3)_4Pb$ and Pb° in acetonitrile [14] (eqn. 9). Similarly unknown CH_3Pb^{3+} (eqn. 2) forms $(CH_3)_2Pb^{2+}$ [9] (eqn. 6). Carbocation donors such as CH_3I or carbanion donors such as $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ (I)** can effect methyl transfers. Two groups [10, 12] have reported $(CH_3)_4$-Pb from the reaction of CH_3I with Pb° in water. Similar reactions with lead(II) salts yield only $(CH_3)_2$-Pb^{2+} as detectable methyllead product. Reactions of (I) with lead(II) and methyllead(IV) ions in acetonitrile [14] and of methylcobalamin with PbO_2 in water [15] both yield $(CH_3)_4Pb$ by a CH_3^- transfer process. Thayer [16] reported demethylation of methylcobalamin by methyllead(IV) compounds but did not identify $(CH_3)_4Pb$. Other workers also failed to identify methyllead products from the above reaction [6, 9, 17].

At present there is uncertainty about the mechanims of methyl transfer to Pb(II) or Pb(IV) species in aqueous media, and the possible pathways (eqns. 2–9) require extensive study. In this work we describe the separate and combined effects of carbanion (complex (I)) and carbocation (CH_3I) donors on methylation of lead(II) in the presence or absence of the MnO_2 oxidizing agent. We also investigated $(CH_3)_4Pb$ formation from reactions of (I) with $(CH_3)_2PbCl_2$ and $(CH_3)_3PbCl$. These reactions are important because they would demonstrate that nucleophilic attack on products of oxidative addition

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**(N_4) is an abbreviation for 2,3,9,10-tetramethyl-1,4,8,-11-tetraazacyclotetradeca-1,3,8,10-tetraene.

reactions (eqns. 1, 2) by naturally occurring carbanion donors would ultimately produce air transportable, hydrophobic, and toxic $(CH_3)_4Pb$. Such processes would complement dismutation of $(CH_3)_2M^{2+}$ and $(CH_3)_3M^+$ (M = Sn, Pb) species that might take place in the environment in the presence of sulphur and oxygen ligands [6, 18–20].

Experimental

Synthesis

All reagents were obtained commercially and used without further purification unless otherwise stated.

$[Co(N_4)Cl_2]ClO_4 \cdot H_2O$ was synthesized by a variation of a literature method [21]. Typically 1,3-diaminopropane·2HCl (11.76 g, 80 mmol) in 30 cm^3 dry methanol was cooled to 2 °C and 2,3-butanedione (7.0 g, 80 mmol) in 20 cm^3 dry methanol was added. The slurry was constantly stirred and KOH (4.48 g, 80 mmol) in 70 cm^3 dry methanol was added slowly, while ensuring that the temperature never exceeded 5 °C. After 30 min a solution of $Co(O_2CCH_3)_2 \cdot 4H_2O$ (10 g, 40 mmol) in 300 cm^3 dry methanol was added. The reaction mixture was stirred at room temperature for 15 h, filtered, and $NaClO_4 \cdot H_2O$ (5.62 g, 50 mmol) in 40 cm^3 dry methanol was added to the filtrate. The resulting gray-green powder was filtered, washed with dry methanol, and dissolved in 300 cm^3 acetonitrile. Concentrated HCl (9 cm^3) was added and crystallization of green $[Co(N_4)Cl_2]ClO_4$ occurred after slow room temperature evaporation of the solvent to half its original volume (30% yield).

Pure $[Co(N_4)Cl_2]ClO_4$ (1.9 g, 4 mmol) was dissolved in a 50/50 mixture of 300 cm^3 acetone and dry methanol while stirring and heating to 50 °C. The mixture was filtered and protected from light. First 3 cm^3 iodomethane (46 mmol) and then sodium borohydride (0.4 g, 1 mmol) dissolved in the minimum amount of water was added dropwise to the filtrate. After 5 min $NaClO_4 \cdot H_2O$ (0.4 g, 3 mmol) in methanol was added, and the red solution was reduced to 30 cm^3 by rotary evaporation at room temperature. A 24% yield of bright red crystals was isolated after cooling to 0 °C for 15 h. $[(CD_3)_2Co(N_4)]ClO_4 \cdot H_2O$ was prepared similarly, using CD_3I. Both complexes were analyzed by elemental analysis and UV spectroscopy.

Manganese dioxide suspension was prepared according to a literature method [22].

Tetraethyllead in toluene from Ethyl Corp. was standardized by dissolving 0.15 g of the toluene/$(CH_3)_4Pb$ mixture in 10 cm^3 of saturated bromine water, boiling with 50 cm^3 of 1.0 M nitric acid, and titrating with EDTA [23].

Trimethyllead chloride, obtained from Ethyl Corp. was purified by sublimation. Dimethyllead(IV) chloride was prepared by a literature method [24].

UV–Visible Spectra

Spectra were recorded on a Cary Model 219 or 14 Spectrophotometer. Spectral titrations were carried out by placing 2.8 cm^3 aliquots of 1×10^{-4} M solution of (I) in 1 cm quartz cells, injecting predetermined amounts of standardized lead solutions, and monitoring absorbance decreases at 436 nm due to the demethylation of (I). Concentrations of aqueous (I) solutions were determined by UV–Visible spectrophotometry (λ_{max} = 436 nm; ϵ = 6800 $cm^{-1} M^{-1}$ [25]).

GC Analysis

Reactions were carried out in the dark at room temperature in 50 cm^3 of aqueous solutions in 60 cm^3 vials sealed with silicon rubber septa. Ionic strength of the reaction media was 0.1 M KNO_3 for Pb^{2+} experiments and 0.1 M KCl for $(CH_3)_2$-$PbCl_2$ and $(CH_3)_3PbCl$ experiments. Head space gases were analyzed after 3 h by sampling with a 0.5 cm^3 gas tight syringe and injecting in a Varian 3700 gas chromatograph with a flame ionization detector (GC-FID). Quantitation of $(CH_3)_4Pb$ was carried out by injecting head space of standards and comparing retention times and peak areas. Reaction products were also identified by mass spectrometry. Methane evolution was quantified using standards produced from the acid hydrolysis of $(CH_3)_2Co(1\text{-}N_4)$, which yields one mol of CH_4 per mol of complex [26]. A Hewlett-Packard 3390A integrator calculated peak areas.

All analyses were carried out in triplicate with peak area relative standard deviation varying between 1.2–23.4% for CH_4 and 0.8–5.6% for $(CH_3)_4Pb$.

The column used for all analyses was a glass column (1,800 mm length, 4 mm i.d.) packed with 10% SP-2100 on Supelcoport 80–100 mesh W-AW-DMCS support. It was kept isothermally at 70 °C with the injection port and detector temperatures at 100 °C. The carrier gas (N_2) flow rate was 30 cm^3 min^{-1} and retention times for CH_4 and $(CH_3)_4Pb$ were 0.64 min and 4.95 min, respectively.

Mass Spectrometry

Mass spectra were recorded on a Hitachi-Perkin Elmer Model RMU60E mass spectrometer and processed by an Apple IIe microcomputer. Head space gases (1 cm^3) were injected directly in the liquid inlet.

Results and Discussion

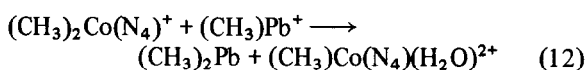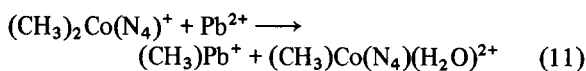Most electrophiles react with (I) by methyl transfer to form solvated $(CH_3)Co(N_4)(SOLV)^{2+}$ (eqn. 10). The second methyl group of (I) does not react

$$(CH_3)_2Co(N_4)^+ + E^+ \longrightarrow$$
$$CH_3E + (CH_3)Co(N_4)(SOLV)^{2+} \qquad (10)$$
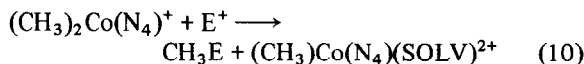
with lead electrophiles under the experiment conditions.

Reactions of lead electrophiles and (I) in various electrophile/(I) mol ratios monitored by visible spectroscopy indicate the approximate times of complete transfer of the first methyl group (eqn. 10). The Pb^{2+} reaction in 1/1 or 1/4 ratios is complete in 2 min. The $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ reactions in 1/4 ratios likewise take 2 min. In contrast the half-life of (I) in water in the absence of lead electrophiles is 24 h, and the products are solvated $(CH_3)Co(N_4)^{2+}$ and CH_4.
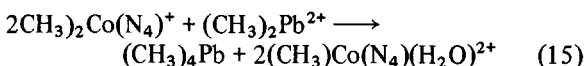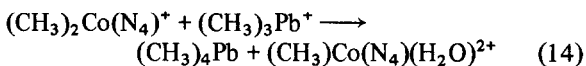
We carried out spectral titrations to determine stoichiometries of the methyl transfer reactions. Endpoint values for Pb^{2+} were 0.6 to 0.7 Pb^{2+}/complex (I). This ratio suggests that Pb^{2+} obtains its first methyl from (I) (eqn. 11), but acceptance of the second methyl from another mol of (I) (eqn. 12) is incomplete. If only reaction 11 occurs, the ratio should be 1/1; if reactions 11 and 12 both

$$(CH_3)_2Co(N_4)^+ + Pb^{2+} \longrightarrow$$
$$(CH_3)Pb^+ + (CH_3)Co(N_4)(H_2O)^{2+} \quad (11)$$

$$(CH_3)_2Co(N_4)^+ + (CH_3)Pb^+ \longrightarrow$$
$$(CH_3)_2Pb + (CH_3)Co(N_4)(H_2O)^{2+} \quad (12)$$

occur, the ratio should be 1/2. The 0.6–0.7 endpoint suggests that reaction 11, but not reaction 12 is complete. Possibly some $(CH_3)Pb^+$ reacts by a different pathway, *e.g.* with water. Neither $(CH_3)Pb^+$ nor $(CH_3)_2Pb$ have been isolated, but indirect evidence for both during reactions of Pb^{2+} with (I) in acetonitrile is strong [14]. In that study intermediate $(CH_3)_2Pb$ quantiatively forms Pb° and $(CH_3)_4Pb$ (eqn. 15):

$$(CH_3)_2Pb \longrightarrow 0.5Pb^\circ + 0.5(CH_3)_4Pb \quad (13)$$
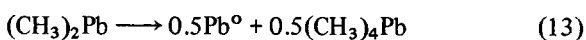
Spectral titrations of (I) with $(CH_3)_3Pb^+$ or $(CH_3)_2Pb^{2+}$ gave easily explainable results. The electrophile/complex (I) mol ratios are 1/1 for $(CH_3)_3Pb^+$ (eqn. 14) and about 1/2 for $(CH_3)_2Pb^{2+}$ (eqn. 14):

$$(CH_3)_2Co(N_4)^+ + (CH_3)_3Pb^+ \longrightarrow$$
$$(CH_3)_4Pb + (CH_3)Co(N_4)(H_2O)^{2+} \quad (14)$$

$$2CH_3)_2Co(N_4)^+ + (CH_3)_2Pb^{2+} \longrightarrow$$
$$(CH_3)_4Pb + 2(CH_3)Co(N_4)(H_2O)^{2+} \quad (15)$$

The above spectrophotometric results demonstrated that reactions of (I) with the three lead electrophiles are over in a few minutes, and that they occur by fairly reproducible stoichiometries. Subsequently we studied reactions of Pb^{2+} with (I) in the presence and absence of CH_3I and MnO_2, and reactions of $(CH_3)_3Pb^+$ or $(CH_3)_2Pb^{2+}$ with (I) in different lead(IV) electrophile/complex (I) ratios.

Previous results show that iodomethane slowly reacts with Pb^{2+} by oxidative addition to form

$(CH_3)_2Pb^{2+}$ [9–11]. In addition Dillard *et al.* [27] reported that MnO_2 nodules may effect surface oxidation of Pb(II) to Pb(IV). For these reasons we designed a factorial experiment to study aqueous methylation of $Pb(NO_3)_2$ by (I). The factorial experiment showed separate and combined effects of complex (I), CH_3I, and MnO_2 (Table I). Only when Pb^{2+} and (I) were present (vials 4, 5, 7, and 10) did we detect $(CH_3)_4Pb$. The low yields of 0.04 to 0.12% emphasize the minor nature of this pathway. We attribute the lower $(CH_3)_4Pb$ yield in the presence of MnO_2 to adsorption of Pb^{2+}. No appreciable adsorption of $(CH_3)_4Pb$ on MnO_2 occurred because a standard $(CH_3)_4Pb$ solution with 20 μmol MnO_2 after 3 h had the same $(CH_3)_4Pb$ head space concentration as that with no MnO_2. The presence of iodomethane did not significantly enhance $(CH_3)_4Pb$ yields in experiments containing complex (I) and Pb^{2+}. We detected no $(CH_3)_4Pb$ in reactions containing only iodomethane and $Pb(NO_3)_2$. These last results are in agreement with observations by other workers of slow aqueous reaction between iodomethane and $Pb(NO_3)_2$ over 21 days and production of $(CH_3)_2$-Pb^{2+} as the only methyllead product [9, 11].

Methylation of $Pb(NO_3)_2$ to $(CH_3)_4Pb$ probably proceeded via an electrophilic attack of Pb^{2+} on (I) and formation of the $(CH_3)_2Pb$ intermediate (eqns. 11–13) in a manner similar to the reaction in acetonitrile [14]. Production of methane in 13 to 15% yield (Table I) is explainable on the basis of eqn. 16,

$$(CH_3)Pb^+ + H_2O \longrightarrow Pb(OH)^+ + CH_4 \quad (16)$$
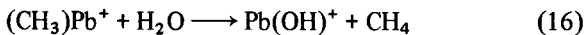
because in the short reaction times of these experiments complex (I) did not appreciably decompose due to its reaction with water. The fate of the majority of the methyl transferred from (I) as observed in the spectrophotometric experiments is unknown. Possibly small amounts of non-volatile $(CH_3)_3Pb^+$ and $(CH_3)_3Pb^{2+}$ or formaldehyde formed by methyl radicals and oxygen are present.

Table II shows that reactions of (I) with low concentrations of $(CH_3)_2Pb^{2+}$ (41 to 82 μmol) and $(CH_3)_2Pb^+$ (84 to 168 μmol) give 33 to 65% yields of $(CH_3)_4Pb$ and 12 to 22% yields of CH_4. Stoichiometric reactions (vials 1 and 4) produced lower amounts of $(CH_3)_4Pb$ than reactions containing a two-fold excess of (I) (vials 2 and 3). Analysis of blanks containing only $(CH_3)_2PbCl_2$, $(CH_3)_3PbCl$ or (I) yielded no detectable $(CH_3)_4Pb$. We used deuterium labelled $[(CD_3)_2Co(N_4)]ClO_4 \cdot H_2O$ under similar reaction conditions to eliminate the possibility of dismutation reactions (eqns. 7, 8) and to establish the origin of methyl groups in $(CH_3)_4Pb$. Identification of $(CH_3)_3Pb(CD_3)$ and $(CH_3)_2Pb(CD_3)_2$ by mass spectrometry confirmed the mechanism of methyl transfer by electrophilic attack on the methyl groups of (I). Furthermore by comparison of

TABLE I. Experimental Setup and Results of 2^3 Factorial Experiment for Methylation of Pb^{2+} [a,b,c]

Vial	Pb^{2+}	$(CH_3)_2Co$	CH_3I	MnO_2	CH_4		$(CH_3)_4Pb$	
					μg	% yield	μg	% yield
4	+	+	+	+	61.0	14.7	2.5	0.05
5	+	+	+	−	56.1	13.5	9.9	0.18
1	+	−	+	+	d		ND	
9	+	−	+	−	d		ND	
7	+	+	−	+	54.5	13.1	2.1	0.04
10	+	+	−	−	58.9	14.2	6.5	0.12
8	+	−	−	+	d		ND	
6	+	−	−	−	d		ND	
2	−	+	+	+	d		ND	
3	−	+	−	+	d		ND	

[a]Abb. + and − denote presence and absence of reagent; ND means not detected at 1 ng cm^{-3} in a 0.5 cm^3 sample, $(CH_3)_2Co$ is $\{(CH_3)_2Co(N_4)\}ClO_4\cdot H_2O$.   [b]Reactions in 50 cm^3 0.1 M KNO_3.   [c]Reagents added: 20.5 μmol $Pb(NO_3)_2$, 41.0 μmol $\{(CH_3)_2Co(N_4)\}ClO_4\cdot H_2O$, 160 μmol CH_3I, and 20 μmol MnO_2.   [d]Not analysed for.

TABLE II. Methane and Tetramethyllead Yields from Methylation of $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ by $\{(CH_3)_2Co(N_4)\}ClO_4\cdot H_2O$.[a]

Vial	Lead reagent, μmol	CH_4		$(CH_3)_4Pb$	
		μg	% yield	μg	% yield
1	0.410 $(CH_3)_2PbCl_2$	1.8	12	40.1	47.0
2	0.205 $(CH_3)_2PbCl_2$	3.4	22	27.6	65.0
3	0.420 $(CH_3)_3PbCl$	3.1	20	53.4	61.4
4	0.840 $(CH_3)_3PbCl$	2.6	18	57.8	33.3

[a]All reactions in 50 cm^3 0.1 M KCl with 0.940 μmol $\{(CH_3)_2Co(N_4)\}ClO_4\cdot H_2O$.

intensities of $^{208}_{82}Pb$ isotopes of m/e values 253 $((CH_3)_3Pb^+)$ and 256 $((CH_3)_2Pb(CD_3)^+)$ in the spectrum of $(CH_3)_3Pb(CD_3)$ established that at least 90% of $(CH_3)_3Pb^+$ present was a product of the fragmentation of $(CH_3)_3Pb(CD_3)$ (intensity ratio 0.296; theoretical value 0.33).

The present work demonstrates that methylation of Pb^{2+} may proceed in aqueous media via its electrophilic attack on (I) (a methyl cobalamin model) with resulting formation of $(CH_3)_4Pb$ in environmentally significant yields. Methylation of $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ proceeds in high yields indicating that partially methylated lead species present in the environment as a result of methylation by carbocation donors or as decomposition products of spilled antiknock additives may be recycled by formation of toxic, air-transportable $(CH_3)_4Pb$.

Acknowledgments

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