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Methylation of tin(II) and lead(II) in sediment by carbanion donors

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A factorial experimental design determined separate and combined effects of $MeCoB_{12}$ (methylcobalamin) and $Me_2Co(N_4)^+$ (a methylcobalamin model) on methylation of Sn(II) and Pb(II) in sediment matrices. Total methyltin yields ranged from 1.4% to 3.2%, and total methyllead yields varied from 0.037% to 0.11%. No methylmetal products occurred in the absence of $Me_2Co(N_4)^+$.

Keywords: Factorial experiment, methylcobalamin, model cobalamins, methyltins, methylleads, methylmetals

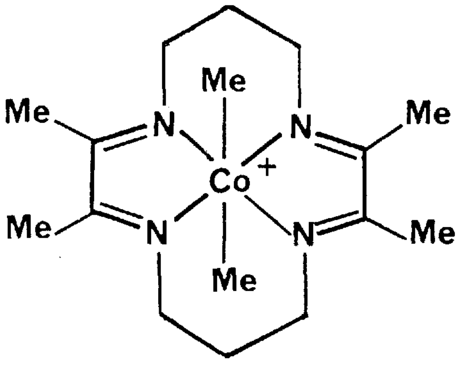
INTRODUCTION

There is much concern about organotin and organolead compounds in the environment. For example, considerable quantities of butyltin compounds, which are widely used as biocides, stabilizers, antifouling agents in paints, and bacteriocides, escape into the environment.[1] Tetraalkyllead compounds are still used in many parts of the world as octane boosting additives, but their use is diminishing. Concern arises over the use of the organotin[1] and organolead[2] compounds because they are considerably more toxic than their inorganic analogs.

It is not at all obvious that methyltin and methyllead compounds in the environment are predominantly anthropogenic in origin. Gilmour et al.[3] convincingly demonstrated methylation of Sn(IV) to $MeSn^{3+}$ in anaerobic sediments. In addition Maguire[4] found in Ontario sediments Bu_3MeSn and Bu_2Me_2Sn that probably form by environmental methylation of butyltin pollutants. The case for environmental methylation of lead is considerably less convincing.[5,6]

Previous work by Weber and co-workers using carbocation and carbanion methyl donors in model systems clearly demonstrated methylation of Sn(II)[7] and Pb(II)[8,9] Craig and Rapsomanikis[10] also demonstrated that methyl iodide methylates tin(II) and lead(II) salts in distilled water to give low yields of various methylmetal products.

This study differs from previous work by quantitating methylation of low concentrations of tin(II) and lead(II) in sediments with only carbanion methyl donors. Use of low metal(II) concentrations is possible because of the group's recent advances in analytical methodology for determination of methyltin compounds[11] and methyllead compounds.[12] The major results are methylation of Sn(II) in reasonable yield and of Pb(II) in low yield, and the predominance of $Me_2Co(N_4)^+$ in the methylation process (N_4 is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene—see Fig. 1).



$[Me_2Co(N_4)]^+$

Figure 1

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EXPERIMENTAL

All reagents were obtained commercially and used without further purification unless stated otherwise. Synthesis of $Me_2Co(N_4)^+$ was described previously.[9] Sediment was from the Great Bay Estuary (NH, USA). Reactions were carried out in $120\,cm^3$ vials sealed with 'crimp on' Teflon-lined silicone septa in the dark at room temperature using 5 g sediment. Tables 1 and 2 list concentrations of all reagents. Gases in head spaces were determined after 5 days by sampling with a $0.5\,cm^3$ gas-tight syringe and injecting into a Varian gas chromatograph with a flame ionization detector coupled with a Hewlett–Packard 3990 peak area integrator. Quantitation of Me_4Sn and Me_4Pb was done by injecting head space samples of standards (after standard addition) and comparing peak areas. Ionic methyltin compounds were determined by a hydride generation–atomic absorption spectrometric method,[11] and ionic methyllead compounds by derivatization by an ethylation–atomic absorption spectrometric method[12] or gas chromatography.

RESULTS AND DISCUSSION

Factorial experimental design

Donard and Weber[13] previously discussed the rationale for factorial design experiments (Tables 1 and 2). This study investigated the presence (10 μmol) or absence of $Me_2Co(N_4)^+$ and $MeCoB_{12}$ as two independent variables on the yields of methylmetal products from tin(II) and lead(II). This 2^2 factorial design, which includes triplicate experiments for error analysis, measures all combinations of the two variables to determine their statistical relevance individually and as combinations. Nondetection of methylmetal products in the absence of methylating agents (--experiments) demonstrated the absence of methylmetal compounds in the sediment.

Possible methylation processes

Initial reactions between a carbanion donor and metal(II) would produce MeM(II) and Me_2M (Eqns. 1 and 2).

$$M(II) + Me^- \rightarrow MeM(II) \qquad [1]$$

$$MeM(II) + Me^- \rightarrow Me_2M(II) \qquad [2]$$

Disproportionation of MeM(II) (Eqn. 3) or $Me_2M(II)$ (Eqn. 4) would produce a methylmetal(IV) compound and M^0.

$$2MeM(II) \rightarrow Me_2M(IV) + M^0 \qquad [3]$$

$$2Me_2M(II) \rightarrow Me_4M + M^0 \qquad [4]$$

Alternatively, if Sn(II) were oxidized to Sn(IV), successive methylation steps by a CH_3^- donor could form mono-, di-, tri-, and tetramethyltin(IV) (Eqn. 5).

Table 1 Experimental design and yields of methyltin compounds[a]

Variables	Levels	
	+	−
A = $Me_2Co(N_4)^+$, μmol	10	0
B = $MeCoB_{12}$, μmol	10	0

		Percent yield[b] (μg)[c]				
A	B	$MeSn^{3+}$	Me_2Sn^{2+}	Me_3Sn^+	Me_4Sn	Total
+	+	0.03 (0.15)	0.08 (0.50)	2.86 (17.0)	0.19 (1.13)	3.16 (18.8)
+	−	nd	nd	1.23 (7.30)	0.19 (1.13)	1.42 (8.43)
−	+	nd	nd	nd	nd	nd
	−	nd	nd	nd	nd	nd

[a] Each experiment contained 5 μmol (595 μg) Sn(II) as $SnCl_2$
[b] Based on Sn(II) added
[c] Limit of detection is 20 pg; nd is not detected

$$M(IV) \xrightarrow[a]{Me^-} MeM(IV) \xrightarrow[b]{Me^-}$$

$$Me_2M(IV) \xrightarrow[c]{Me^-} Me_3M(IV) \xrightarrow[d]{Me^-} Me_4M(IV) \qquad [5]$$

Such a process is unlikely for lead because of its high oxidation potential and instability of monomethyllead(IV). Ionic methylmetal(IV) compounds formed could undergo redistribution reactions (Eqns. 6, 7, and 8).

$$2MeM(IV) \rightarrow Me_2M(IV) + M(IV) \qquad [6]$$

$$2Me_2M(IV) \rightarrow Me_3M(IV) + MeM(IV) \qquad [7]$$

$$2Me_3M(IV) \rightarrow Me_4M + Me_2M(IV) \qquad [8]$$

Methylation of tin(II)

Table 1 contains mean values for percent conversion of tin(II) to methyltin products. Detectable methyltin yields of all methyltin products occur when $Me_2Co(N_4)^+$ and $MeCoB_{12}$ are present, tri- and tetramethyltin occur with $Me_2Co(N_4)^+$ alone, and no products occur with $MeCoB_{12}$ alone. Although the presence of $MeCoB_{12}$ with $Me_2Co(N_4)^+$ resulted in larger yields of tri- and tetramethyltin than $Me_2Co(N_4)^+$ alone, analysis of variance of three replicates of each experiment proved that at the 95% confidence level the presence of $MeCoB_{12}$ contributed only to production of Me_3Sn^+. However, lack of methyltin products in the absence of $Me_2Co(N_4)^+$ proves that $MeCoB_{12}$ does not methylate Sn(II) in these experiments. Other workers, in contrast, observed methylation of Sn(II) by $MeCoB_{12}$ in a model system.[14]

The major product from methylation of tin is trimethyltin(IV), and it is reasonable to emphasize rationalization of its presence. The most likely path to its formation is methylation of Sn(II) (Eqn. 1), its disproportionation to dimethyltin(IV) and tin metal (Eqn. 3), and methylation of dimethyltin(IV) to trimethyltin(IV) (Eqn. 5, step *c*). This series of reactions also explains the low concentrations of monomethyl- and dimethyltin. Tetramethyltin could originate from carbanion attack on trimethyltin (Eqn. 5, step *d*) or by conversion of trimethyltin to tetramethyltin (Eqn. 8).[15,16] Oxidation of Sn(II) to Sn(IV) followed by successive carbanion attacks (Eqn. 5) is unlikely to produce tri- and tetramethyltin as major products.[7]

Methylation of lead(II)

Methylation of lead(II) under the same conditions used for tin resulted in very low yields of di-, tri-, and tetramethyllead (Table 2). Methyllead yields are approximately 10^2 times lower than methyltin yields. Yields in the presence of $Me_2Co(N_4)^+$ and $MeCoB_{12}$ are lower than with $Me_2Co(N_4)^+$ alone, but the decrease is insignificant at the 95% confidence level. No methyllead compound was detectable with $MeCoB_{12}$ alone.

Table 2 Experimental design and yields of methyllead compounds[a]

Variables	Levels	
	+	–
A = $Me_2Co(N_4)^+$, μmol	10	0
B = $MeCoB_{12}$, μmol	10	0

		Percent yield × 10^2 [b] (μg)[c]			
A	B	Me_2Pb^{2-}	Me_3Pb^+	Me_4Pb	Total
+	+	1.4 (0.14)	1.9 (0.20)	0.4 (0.04)	3.7 (0.38)
+	–	6.2 (0.65)	4.4 (0.46)	0.5 (0.05)	11.4 (1.18)
–	+	nd	nd	nd	nd
–	–	nd	nd	nd	nd

[a] Each experiment contained 5 μmol (1040 μg) Pb(II) as $Pb(NO_3)_2$

[b] Based on Pb(II) added

[c] Limit of detection is 20 pg; nd is not detected

Methyllead products probably form via disproportionation of MePb(II) (Eqn. 3) and $Me_2Pb(II)$ (Eqn. 4) followed by successive methylation of di- and trimethyllead (Eqn. 5, steps *c* and *d*). Rapsomanikis et al.[9] found low yields of tetramethyllead after reactions of $Me_2Co(N_4)^+$ with Pb(II) in aqueous KNO_3. In that paper, use of deuterated methyl groups on cobalt followed by mass spectral analysis proved that methylation of di- and trimethyllead occurred via methyl transfer from $Me_2Co(N_4)^+$ and not by redistribution of the starting methyllead compounds (Eqns. 6 to 8).

CONCLUSIONS

These results, especially relatively high yields of methyltin products, agree with the concensus that methyltin compounds are predominantly formed within the environment. The low yields of methyllead products are insufficient to clarify the controversy over their possible formation in sediments.

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