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Biomethylation of Tl(I) Compounds

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In a previous paper [1] we showed that microorganisms can methylate Pb^{2+} under anaerobic conditions to give Me_4Pb (Me = CH_3). We therefore decided to examine whether Tl^+, isoelectronic to Pb^{2+} is also amenable to biomethylation by microorganisms and – if Tl^+ is biomethylated – it also increases its formal oxidation number. This question was of great interest, since biomethylation of Pb^{2+} was the only example of an *in vivo* methylation during which the formal oxidation number of the metal ion is increased. During biomethylation of mercury compounds [2] (Hg being the other neighbour of Tl in the periodic system) there is no change of the oxidation state.

Information about experiments on biological transformation of thallium is scarce. It was shown that methyl-vitamin B_{12} can be demethylated *in vitro* by Tl(III) [3, 4], but not by Tl(I) [3]. however the nature of the methylated Tl species has apparently not been established (from spectral titrations it was concluded that $MeTl^{2+}$ is a product of the demethylation of Me-cobaloxime by Tl^{3+}; there were no indications of the formation of Me_2Tl^+ [5]). From experiments with methyl mercury it was suggested [6] that thallium (no oxidation number given; obviously Tl(III) [7]) will be methylated in the environment. The possibility of Tl(I)-transformation by an aerobic bacteria culture, albeit with no specification of active Tl-containing agents, was mentioned in a preliminary transport study [8].

Corresponding to our experiments [1] on the biomethylation of Pb^{2+} we incubated (in 250 ml gas wash bottles in an N_2 atmosphere and under exclusion of O_2 and light) bacteria from the anaerobic sediment of a natural small lake in 100 ml dilution water [9, 10] with added nutrient* for 10 days at 30 °C. During this time – starting on the third day – TlOAc (OAc = acetate) was added in portions up to a maximum concentration of 1g/l. 1.9 g $CaCO_3$ were added to neutralize the acid produced by metabolic processes. After 7 to 21 days 10 ml samples were taken, filtered through a diaphragm and analyzed. The filtered solution contained small amounts of Me_2Tl^+ besides Tl(I). Me_2Tl^+ was complexed with 1-(2-pyridylazo)-2-naphthol (PAN), after masking Tl(I) with EDTA. The Me_2Tl^+–PAN complex was extracted with $CHCl_3$ at pH 10–12 and determined spectrophotometrically at 570 nm [11]. The results showed that, using solution I*, after 14 and 21 days 3 and 10 μg Me_2Tl^+/ml respectively had been formed. Using solution II* 36 μg Me_2Tl^+/ml were detected after 21 days; this corresponds to a conversion of Tl^+ to Me_2Tl^+ of about 3%. However in experiments with peptone as nutrient (meat extract, Merck) only about 1–2 μg Me_2Tl^+/ml were formed after 21 days. This lower yield when using peptone as nutrient agreed with our experience gained during biomethylation of Pb^{2+}. Me_2Tl^+ was the only methylated Tl-species detected. This is understandable in view of the normal behaviour of alkylthallium compounds: monomethylthallium compounds in general are unstable [12] and Me_3Tl decomposes instantaneously in water to form Me_2TlOH and CH_4 [13]. Me_2Tl^+ is stable in aqueous solution.

The experiments do not allow to propose a certain mechanism of the biological transformation of Tl^+ to Me_2Tl^+. Various pathways are conceivable. Methylation of Tl^+ (*e.g.* by Me^- from methyl-vitamin B_{12} [7]) would give MeTl, which however is unknown. We could not detect elementary Tl in the samples, so that it can be concluded that Me_2Tl^+ is not formed by disproportionation of an intermediate MeTl. We now try to find out, whether Tl^+ – in complexed form – is methylated by a CH_3^- donor (methyl-vitamin B_{12}) and simultaneously oxidized by an appropriate electron acceptor (eventually involving radical intermediates) or whether electrophilic attack by CH_3^+ might be responsible for the formation of a monomethylthallium(III) derivative as a primary product; monomethylthallium(III) compounds can either redistribute producing Me_2Tl^+ [14], or might be methylated to Me_2Tl^+ (or to Me_3Tl, which would however hydrolyze to give Me_2Tl^+). We recently showed using alkyllead compounds, that direct biomethylation of alkylmetal compounds is also feasible in principle [15].

Me_2Tl^+ compounds are less toxic to bacteria than Tl^+, so biomethylation of Tl^+ would result in a detoxification of the bacterial environment. This must however not of necessity be the determining reason for the occurrence of the methylation, as biomethylation of Pb^{2+} leads to Me_4Pb, which is much more toxic to bacterial cultures than lead(II) compounds [15].

No methylation of Tl^+ has been observed under aerobic conditions.

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*In 100 ml dilution water [9, 10] had been dissolved: 0.052 g $K_2HPO_4 \cdot 3H_2O$, 0.01 g $MgCl_2 \cdot 6H_2O$, 0.1 g NH_4Cl and either 1.0 g C_2H_5OH (Solution I) or 1.0 g $Ca(OAc)_2$ (Solution II).

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