

# Chemiluminescence from the reaction of tin(II) with tris(2,2'-bipyridyl)ruthenium(III)

Michelle E. Gange,<sup>a</sup> Simon C. Parratt,<sup>b</sup> Philip Jones,<sup>c</sup> Paul S. Francis<sup>a</sup> and Neil W. Barnett<sup>\*a</sup>

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**Unlike many other metal and metalloid ions, tin(II) elicits intense, analytically useful chemiluminescence upon reaction with tris(2,2'-bipyridyl)ruthenium(III) in acidic aqueous solution. This finding provides new insight into the nature of this widely used reagent and has enabled the first direct, selective determination of a metal ion with tris(2,2'-bipyridyl)ruthenium(III).**

During the four decades since the pioneering work of Hercules and Lytle,<sup>1</sup> tris(2,2'-bipyridyl)ruthenium(III) (Ru(bipy)<sub>3</sub><sup>3+</sup>) has become one of the most widely used chemiluminescence/electrochemiluminescence reagents for a diverse range of organic analytes.<sup>2-6</sup> However, very few reports have appeared on the detection of inorganic species, due to either very low or no light emitted from such reactions. The indirect detection of metal ions has been achieved using the formation of emetine-dithiocarbamate metal complexes followed by their reaction with the reagent,<sup>7,8</sup> inhibition of electrochemiluminescence from Ru(bipy)<sub>3</sub><sup>2+</sup> and ethylenediaminetetraacetic acid (EDTA) due to binding with the co-reactant,<sup>9</sup> and the interaction of metals with crown ether-derivatised tris(2,2'-bipyridyl)ruthenium(II) (Ru(bipy)<sub>3</sub><sup>2+</sup>), which altered the quantum yield.<sup>10-12</sup>

We have compared the relative chemiluminescence response from direct reactions between Ru(bipy)<sub>3</sub><sup>3+</sup> and a variety of metal and metalloid species, using flow injection analysis.† The reagent was prepared by oxidation of Ru(bipy)<sub>3</sub><sup>2+</sup> using lead dioxide (and maintained in that state using a recirculating system<sup>13</sup>), before injection into a 0.05 M sulfuric acid carrier stream that merged with the analyte solutions. The relative responses are shown in Table 1.

Each compound reduced the Ru(bipy)<sub>3</sub><sup>3+</sup> complex, which was observed visually as the colour of the solution changed from green to orange. This was attributed to the oxidation of the metal or metalloid species in all cases except for potassium bromide and potassium iodide, where the halide anion was most probably oxidised to the free halogen.<sup>14</sup> Although several species produced detectable chemiluminescence upon reaction with Ru(bipy)<sub>3</sub><sup>3+</sup>, only tin(II) elicited an intense emission that was visually observable in a darkened room. The spectral distribution of this emission matched that of chemiluminescence from the reaction of Ru(bipy)<sub>3</sub><sup>3+</sup> with organic analytes.<sup>15</sup>

The reason for the relatively strong response from tin(II) was not immediately apparent, but a light-producing pathway that rationalises this remarkable selectivity can be postulated by considering the

nature of this analyte in solution and the reaction of Ru(bipy)<sub>3</sub><sup>3+</sup> with organic compounds, such as organic acids and tertiary amines.<sup>16,17</sup> These studies have focussed on two model compounds: oxalate and tripropylamine. In both cases, there is evidence for the initial formation of a radical intermediate that reacts with the reagent to produce the excited ruthenium(II) complex. For example, the proposed mechanism for the reaction between the oxalate anion and Ru(bipy)<sub>3</sub><sup>3+</sup> is shown in Scheme 1.

An analogous mechanism involving the production of a high-energy intermediate can not be derived for most simple metal ions, but in acidic solutions containing complexing anions the predominant tin(II) species are the pyramidal [SnX<sub>3</sub>]<sup>-</sup> ions (e.g. X = Cl<sup>-</sup> in hydrochloric acid solution).<sup>19</sup> There is also evidence for the formation of complexes such as [Sn(SO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> in solutions of sulfuric acid.<sup>19</sup> Single-electron oxidation of these species with Ru(bipy)<sub>3</sub><sup>3+</sup> would therefore produce highly-reactive tin(III) radical anions, which (in a similar manner to the proposed intermediates of the organic analytes<sup>18</sup>) may be responsible for the production of the electronically excited [Ru(bipy)<sub>3</sub><sup>2+</sup>]<sup>\*</sup> and associated luminescence (Scheme 2).

Tin(III) species have been identified in acidic solution at room temperature by UV-absorption (after flash photolysis of tin(II) complexes)<sup>20,21</sup> and in adamantane at low temperatures using electron spin resonance,<sup>22</sup> and proposed as intermediates in the reaction of tin(II) with other single-electron oxidants.<sup>23,24</sup> However, direct detection of radical intermediates under the conditions required for this chemiluminescence is complicated by the speed of the reaction and the relatively low concentration of the intermediate species.‡

As with the proposed light-producing pathways for organic compounds, the chemiluminescence intensity will be highly dependent on the production and nature of the reactive intermediate. To explore the relative response from different tin(II) species, the

**Table 1** Relative chemiluminescence response from metal species (10 mM metal ion in 0.05 M H<sub>2</sub>SO<sub>4</sub> unless otherwise stated) with Ru(bipy)<sub>3</sub><sup>3+</sup>

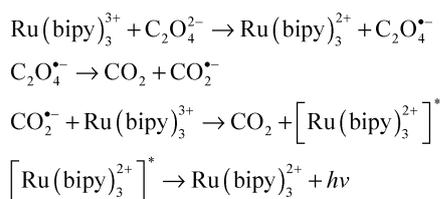
Blank (0.05 M H <sub>2</sub> SO <sub>4</sub> )		0.11
Arsenic(III) chloride <sup>a</sup>	AsCl <sub>3</sub>	0.10
Chromium(III) chloride	CrCl <sub>3</sub>	0.22
Copper(I) chloride	CuCl	0.37
Iron(II) sulfate	FeSO <sub>4</sub>	0.00
Potassium hexacyanoferrate(II)	K <sub>4</sub> Fe(CN) <sub>6</sub>	0.00
Potassium bromide	KBr	0.42
Potassium iodide	KI	0.11
Manganese(II) chloride	MnCl <sub>2</sub>	1.30
Sodium arsenite	NaAsO <sub>2</sub>	0.37
Sodium selenite	Na <sub>2</sub> SeO <sub>3</sub>	0.78
Antimony(III) oxide	Sb <sub>2</sub> O <sub>3</sub>	0.60
Tin(II) chloride	SnCl <sub>2</sub>	100.00

<sup>a</sup> 1000 ppm standard solution in 1 M HCl.

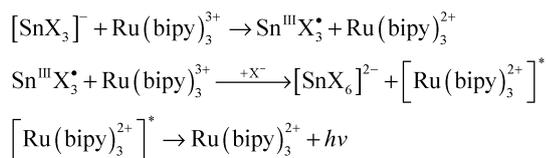
<sup>a</sup>School of Life and Environmental Sciences, Deakin University, Geelong, Victoria 3217, Australia. E-mail: barnie@deakin.edu.au; Fax: +61 3 5227 1040; Tel: +61 3 5227 1409

<sup>b</sup>Kardinia International College, Geelong, Victoria 3220, Australia

<sup>c</sup>Department of Environmental Science, University of Plymouth, Plymouth, Devon, UK PL4 8AA



**Scheme 1** Mechanism for the reaction with oxalate, proposed by Rubinstein and Bard.<sup>18</sup>



**Scheme 2** Proposed mechanism for the reaction between tin(II) halides and tris(2,2'-bipyridyl)ruthenium(III).

reaction was performed in solutions containing a large excess of different sodium halide salts. § At pH 5.5, using an analyte concentration of  $1 \times 10^{-3}$  M, the relative chemiluminescence intensity for NaF, NaCl, NaBr or NaI was 100, 68, 78 and 0.09, respectively. Speciation plots for these systems (using analyte concentrations of  $1 \times 10^{-3}$  M and  $1 \times 10^{-5}$  M) revealed that when 0.05 M NaF was added and the pH adjusted to 5.5, approximately 95% of the tin(II) would be present as the trifluoro anion. ¶ In the case of 0.05 M NaCl or NaBr under the same conditions, the predominant tin species were tin(II) hydroxide and tin(II) acetates.

Precipitation was observed when chloride, bromide and iodide were added to the tin(II) sulfate, which we attributed to the formation of hydroxides. This also occurred when preparing standard solutions of tin halides (at pH 5). A fine white precipitate was observed in SnCl<sub>2</sub> solutions within one hour, faster with SnBr<sub>2</sub>, and almost instantaneous with SnI<sub>2</sub>. No precipitation was observed in solutions of SnF<sub>2</sub> over two hours.

The analytical utility of the chemiluminescence reaction between tin(II) and  $5 \times 10^{-4}$  M Ru(bipy)<sub>3</sub><sup>3+</sup> was explored using flow injection analysis. § Nine tin(II) fluoride standard solutions, ranging in concentration from  $5 \times 10^{-6}$  M to  $2.5 \times 10^{-4}$  M, were prepared in the same solution as that used in the carrier stream (0.05 M NaF and 0.05 M acetate buffer) and degassed with nitrogen to avoid oxidation. Under these conditions, a pH of approximately 5.0 produced the greatest emission intensities (after subtraction of the blank responses). The limit of detection was  $5 \times 10^{-6}$  M and the linear calibration range ( $R^2 = 0.9974$ ) extended to the highest standard tested. Using  $7.5 \times 10^{-5}$  M tin(II) fluoride, the relative standard deviation for 10 replicate injections of the Ru(bipy)<sub>3</sub><sup>3+</sup> reagent was 1.4%.

In a preliminary application of this chemistry, we determined tin(II) in toothpaste – a complex heterogeneous matrix comprising many ingredients, such as abrasives, surfactants, humectants, binders, colours and flavours.<sup>25</sup> Tin(II) is added to toothpastes in various forms (such as the fluoride, gluconate and pyrophosphate) due to the ability of the metal ion to prevent gingivitis, plaque and microbial growth, and in the case of tin(II) fluoride, as a source of water-soluble fluoride.<sup>25,26</sup> A large amount of research has been conducted on the stability and taste of tin(II) compounds in toothpastes.<sup>27</sup> Tin(II) reacts with oxygen to form tin(IV), which reduces the effectiveness of the

**Table 2** Relative chemiluminescence response from toothpaste components (dissolved in aqueous solution) with Ru(bipy)<sub>3</sub><sup>3+</sup>

Samples	Conc. (% m/m)	
Tin(II) fluoride	0.454	100.00
Sodium saccharin	0.2	-0.01
Sodium hexametaphosphate	1	0.07
Sodium lauryl sulfate	1	1.48
Tetrasodium pyrophosphate	1	0.16
Trisodium phosphate	1	0.02
Potassium nitrate	5	0.11
Sorbitol	35	0.87
Glycerol	50	0.98

dental products over time. A simple and accurate method for the determination of soluble tin(II) is therefore required to ensure optimum effectiveness and reliability of these formulations.

The relative chemiluminescence response from various species in toothpastes was examined (Table 2). At the approximate concentrations found in commercial products, none of the tested components produced a signal that would interfere in the analysis. Nevertheless, a significant blank signal was observed from commercial toothpaste samples after the tin(II) was oxidised to tin(IV) (which does not produce light with Ru(bipy)<sub>3</sub><sup>3+</sup>) by bubbling air through the sample solution overnight. Pyrophosphate can form strong complexes with tin(II), but speciation plots showed that under the analytical conditions (0.05 M sodium fluoride, 0.05 M acetate buffer, pH 5.0), complexation with pyrophosphate was negligible. ¶

Prior to sample collection, the first 5 cm of toothpaste from the tube was discarded, to avoid material previously exposed to air. An accurately weighed sample was made into a slurry (using the buffer solution, which had been bubbled with nitrogen overnight) and centrifuged for 10 min. The supernatant was diluted further with the buffer solution and a chemiluminescence signal obtained using flow injection analysis. Samples were then oxidised by bubbling with air overnight to establish the blank response. The blank-corrected results for two commercially available toothpastes containing tin(II) fluoride were in reasonable agreement with those obtained using a redox titration with potassium iodate (1.06 and 1.10 mg/g, and 0.91 and 0.88 mg/g, respectively), considering the time required for analysis and the limited stability of the analyte in aqueous solution. || Unlike contemporary methodology, this chemiluminescence approach is well suited for the detection of tin(II) after chromatographic separation and we are currently examining the utility of such systems for the determination of this analyte in a variety of consumer products with complex matrices.

## Notes and references

† The flow injection analysis manifold with chemiluminescence detector was constructed from a Gilson Minipuls 3 peristaltic pump (John Morris Scientific, Australia) with PVC pump tubing (1.02 mm i.d., Protech Group, Australia) and a Valco six-port injection valve (SGE, Australia) with a 70 µL sample loop. The chemiluminescence detector consisted of a spiral PTFE tubing flow-cell positioned against a photomultiplier tube (Electron Tubes, UK) operated at 900 V provided by a stable power supply and voltage divider (Electron Tubes models PM28B and C611; ETP, Australia). The output from the photomultiplier tube was converted by a transimpedance amplifier (Electron Tubes model A1; ETP) and recorded on a strip chart recorder (Yokogawa Electric Works, Japan). The tris(2,2'-bipyridyl)ruthenium(III) reagent ( $1 \times 10^{-3}$  M in 0.05 M H<sub>2</sub>SO<sub>4</sub>)

was injected into a carrier stream that merged with the analyte/sample stream immediately prior to the point of detection.

‡ Mechanisms for the chemiluminescence reactions of Ru(bipy)<sub>3</sub><sup>3+</sup> with potassium oxalate and tripropylamine were postulated many years ago,<sup>18,28</sup> and have been further developed and have become widely accepted.<sup>5,6</sup> However, direct evidence for the tripropylamine radical cation under relevant conditions was not obtained until 2002.<sup>29</sup> The oxalate radical anion (C<sub>2</sub>O<sub>4</sub><sup>•-</sup>) is yet to be detected in reactions of Ru(bipy)<sub>3</sub><sup>3+</sup> with potassium oxalate.

§ The Ru(bipy)<sub>3</sub><sup>3+</sup> reagent was injected into a carrier stream containing 0.05 M sodium halide, which then merged with a tin(II) solution prepared from SnSO<sub>4</sub> and 0.05 M sodium halide. The pH of the reaction mixture was set by adding 0.05 M acetate buffer to the carrier and analyte solutions. The sample loop was filled manually using a syringe (rather than the previously described recirculating system), to avoid contamination of the reagent reservoir.

¶ Medusa metal speciation software was developed by Ignasi Puigdomenech, formerly with the Royal Institute of Technology (KTH), Stockholm, Sweden. The database for this study was constructed by Phil Jones using information from the NIST Standard Reference Database.<sup>30</sup>

|| The iodate titration was based on the method of Jamieson<sup>31</sup> with some alterations. Samples were prepared as for chemiluminescence analysis, except that the solvent was a 50:50 mixture of concentrated hydrochloric acid and deionised water that was degassed overnight by bubbling with nitrogen. The sample solution (25 mL) and chloroform (1 mL) were transferred into a conical flask. The sample was titrated against 0.01 M potassium iodate in water, until loss of the pink colour from the chloroform layer.

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