

# Chromogenic reagent for mercury based on Kemp's acid imide

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## Kemp's acid imide type chromogenic reagent showed a significant colour change with excellent selectivity for Hg<sup>II</sup> over other transition- and heavy-metal ions.

Recently, we reported that Kemp's acid imides were useful carriers for the transport of various metal ions.<sup>1,2</sup> Amongst these carriers, the aromatic Kemp's acid imide **2** had an especially high transport ability and efficiency for Hg<sup>II</sup>. By substituting a chromogenic moiety in place of the *n*-butyl group of **2**, a molecular sensor for mercury was constructed. Here, we present an excellent chromogenic reagent **1**, which is different from the usual reagents having either sulfur atoms or a macrocyclic structure,<sup>3–5</sup> for Hg<sup>II</sup> with high selectivity over other transition- and heavy-metal ions.

Chromophore **1** was synthesized in 59% yield in the same manner as **2** by the reaction of Kemp's triacid anhydride acid chloride and *N,N*-dimethyl-4,4'-azodianiline **3**.<sup>6</sup> Characterization of **1** was accomplished using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. UV–VIS spectra were measured on a Jasco V-550 spectrophotometer in acetonitrile containing 0.01 mol dm<sup>-3</sup> LiClO<sub>4</sub> as electrolyte; a large excess of LiClO<sub>4</sub> did not affect the spectra of **1** under these conditions. A 1.00 cm optical pathlength quartz cell, stirred magnetically, and thermostatted at 25.0 ± 0.2 °C, was used in the spectral measurements.

The titration experiments were carried out using 3.00 × 10<sup>-5</sup> mol dm<sup>-3</sup> of chromophore **1**, with the addition of 0.0–10.0 mol equiv. of Hg(ClO<sub>4</sub>)<sub>2</sub>. After the addition of an acetonitrile solution of Hg(ClO<sub>4</sub>)<sub>2</sub>, the yellow chromophoric solution (λ<sub>max</sub> = 418 nm) dramatically changed colour to red with the appearance of a new peak (λ<sub>max</sub> = 519 nm), as shown in Fig. 1. As clearly seen upon the addition of Hg<sup>II</sup> from 0.0 to 10.0 mol equiv. the original absorption band (λ<sub>max</sub> = 418 nm) intensity decreased, while the new absorption band (λ<sub>max</sub> = 519 nm) intensity increased. The two absorption bands, with an isosbestic point at 462 nm, indicated an equilibrium between at least two species. The simplest case would involve two species present in solution, assumed to be the chromophore itself (λ<sub>max</sub> = 418 nm), and the complex (λ<sub>max</sub> = 519 nm) in a 1 : 1 (and/or 2 : 2) chromophore : metal ratio. The 1 : 1 (and/or 2 : 2)

complex was also proposed by <sup>13</sup>C NMR titration of **2**.<sup>1</sup> Moreover, **1** showed a significant response to Hg<sup>II</sup> cation at concentrations as low as 4.0 × 10<sup>-6</sup> mol dm<sup>-3</sup>. Assuming 1 : 1 complexation of Hg<sup>II</sup>, the stability constant derived from the absorption spectral data was 8.0 × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup>.

The same experiments were also carried out using different metals, and the results summarized in Table 1. Clearly, **1** is the most sensitive to Hg<sup>II</sup> among the transition- and heavy-metal ions studied. The sensitivities of Zn<sup>II</sup> and Cd<sup>II</sup> with respect to Hg<sup>II</sup> are 1/75 and < 1/7500, respectively. It is very interesting that **1** has high selectivity towards highly toxic mercury over the biologically important zinc cation.<sup>7</sup> Although the detectable concentration limit of **1** was not as low as dithizone,<sup>4</sup> which is the usual chromogenic reagent for mercury, its selectivity for mercury was very high, even though it contains no sulfur atom unlike most other mercury selective chromophores.<sup>3,4</sup> The high selectivities (sensitivities) shown in Table 1 show that no preorganization of a suitable cavity seems to be necessary for ideal complexation as discussed by Lerchi *et al.*<sup>3</sup> The selectivity is similar to that previously reported in the transport results of imide **2**.<sup>1</sup> The only unusual phenomenon was observed in the

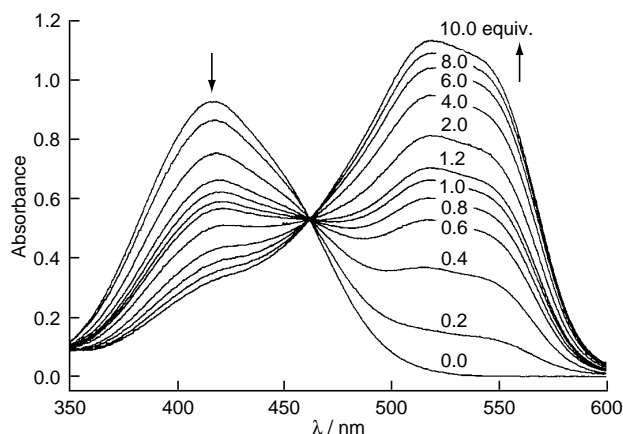
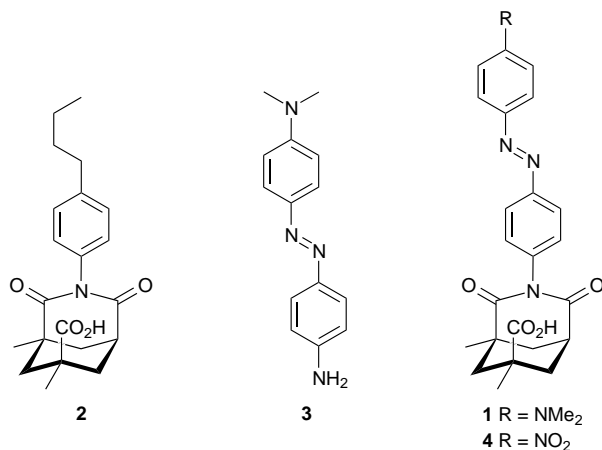


Fig. 1 UV–VIS spectra of **1** (3.00 × 10<sup>-5</sup> mol dm<sup>-3</sup>) and upon incremental addition of Hg(ClO<sub>4</sub>)<sub>2</sub> in MeCN containing 0.01 mol dm<sup>-3</sup> LiClO<sub>4</sub> as electrolyte

Table 1 Detection limits (mol dm<sup>-3</sup>) of **1**<sup>a</sup>

Metal ion <sup>b</sup>	10 <sup>4</sup> c/mol dm <sup>-3</sup>	Selectivity ([M]/[Hg])
Hg <sup>II</sup>	0.040	1.0
Cd <sup>II</sup>	> 300	> 7500
Zn <sup>II</sup>	3.0	75
Co <sup>II</sup>	9.0	230
Ni <sup>II</sup>	30	750
Cu <sup>II</sup>	0.15	3.8
Pb <sup>II</sup>	0.12	3.0
Ag <sup>I</sup>	16	400

<sup>a</sup> 3.00 × 10<sup>-5</sup> mol dm<sup>-3</sup> in MeCN containing 0.01 mol dm<sup>-3</sup> LiClO<sub>4</sub> as electrolyte at 25.0 ± 0.2 °C. <sup>b</sup> The counter anion was ClO<sub>4</sub><sup>-</sup> except for Cd(NO<sub>3</sub>)<sub>2</sub>.



UV–VIS spectra in titration with Cu<sup>II</sup>. In this case, in addition to the new absorption band ( $\lambda_{\text{max}} = 519 \text{ nm}$ ), another ( $\lambda_{\text{max}} = 610 \text{ nm}$ ) also appeared (not shown). The maximum absorbance at 519 nm was reached upon the addition of 1 mol equiv. of Cu<sup>II</sup>. However, further addition of Cu<sup>II</sup> decreased the 519 nm absorption and increased the new absorption at 610 nm until 2.0 mol equiv. of Cu<sup>II</sup> was added. We propose that this new absorption band arises from the interaction between excess Cu<sup>II</sup> and the dimethylamino group of chromophore **1**, as a consequence of the higher affinity of Cu<sup>II</sup> for nitrogen compared to other metal cations investigated.

The time-dependent spectra of **1** and **3** in the presence of 1 mol equiv. Hg<sup>II</sup> were taken over a period of 5–60 min to elucidate the spectroscopic features of chromophore **1**. These spectra showed that although **3** showed large absorbance changes with time, no spectral change was observed for **1** under the same conditions. In other words, there was no time dependence for the interaction of Hg<sup>II</sup> cation and chromophore **1**.

In order to investigate the mechanism of colour change, hydrochloric acid and sodium hydroxide solution were used in place of Hg<sup>II</sup>, the complexation of Kemp's acid imide **2** with Na<sup>+</sup> is very weak<sup>2</sup> while the spectrum of the 1 : 1 chromophore–HCl solution was exactly the same as that of the 1 : 1 chromophore–Hg<sup>II</sup> solution. This meant **1** was also a good molecular sensor for acid. On the other hand, when an NaOH solution was put into the above solution, the absorption at 519 nm decreased, and disappeared upon addition of 1 equiv. of NaOH. This suggested that protonation played a very important role in changing the colour. A plausible mechanism for the colour change is that when transition- or heavy-metal ions are added to the chromophoric solution, the carboxylic acid proton is removed during complex formation, and that this proton binds to the azo group, changing the conjugate feature of **1**, while the dimethylamino group acts as an electron donating group aiding protonation. This mechanism of the colour change is different from other ionizable cyclic or bicyclic molecular sensors.<sup>5</sup> To obtain further evidence, the nitro-substituted derivative **4** was also prepared. Since the nitro group acts as an electron attracting group which decreases the electronic density at the azo group,

the released proton cannot interact with the azo group to change the conjugate feature of **4**, such that, as predicted, no colour change occurred even in the presence of excess metal ion.

In summary, a novel Kemp's acid imide **1** was prepared as a chromogenic reagent for Hg<sup>II</sup>. The selectivity of **1** for Hg<sup>II</sup> was very high over that of other transition- and heavy-metal ions such as Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Pb<sup>II</sup> and Ag<sup>I</sup>. The mechanism of the colour change was demonstrated as being due to the formation of a complex in 1 : 1 (and/or 2 : 2) chromophore : metal ratio after the addition of the transition- or heavy-metal ion to the chromophoric solution. The complexation causes proton transfer from the carboxyl group to the azo group, changing the colour of the original chromophore **1**.

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