

Research Article

A Selective Chemosensor for Mercuric Ions Based on 4-Aminothiophenol-Ruthenium(II) Bis(bipyridine) Complex

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A new ruthenium(II) complex (cis-ruthenium-bis[2,2'-bipyridine]-bis[4-aminothiophenol]-bis[hexafluorophosphate]) has been synthesized and characterized using standard analytical and spectroscopic techniques, FTIR, ¹H and ¹³C-NMR, UV/vis, elemental analysis, conductivity measurements, and potentiometric titration. Investigation of the synthesized complex with metal ions showed that this complex has photochemical properties that are selective and sensitive toward the presence of mercuric ion in aqueous solution. The detection limit for mercuric ions using UV/vis spectroscopy was estimated to be ~ 0.4 ppm. The results presented herein may have an important implication in the development of a spectroscopic selective detection for mercuric ions in aqueous solution.

1. Introduction

Chemosensors that are selective for specific targets of metal ions are continuously demanded. An especially important category of chemosensors are those targeting toxic heavy metal ions. Mercury in particular is a toxic metal, which when accumulates in the vital organs of human and animals causes poisonous effects that cause serious hematological destruction, such as kidney malfunctioning and brain damage [1–3]. Therefore, monitoring and precise determining of mercuric ion concentration in water and thus in relevant biological matrices are extremely beneficial for the environmental and toxicological monitoring. Despite the increasing efforts for developing low cost methodologies for mercuric detection in aqueous solutions [4–16], the tailored design of new mercuric-colorimetric chemosensors that work effectively in aqueous media remains a key challenge. Up to now the great effort of researchers in this field is directed toward the development of new selective chemosensors based on fluorescence property [17–33]. This is of course due to many advantages in characterizing this

category of chemosensors, at top of which are the high selectivity and sensitivity toward targeted metal ions. Although these fluorometric sensors have been employed enormously in this field, the colorimetric sensing [8, 28, 34–36] of metal ions has been shown to be less laboursome and intensive alternative to fluorescence techniques. The strong thiophilicity of mercury is the most attractive property that is usually taken into account when designing mercury detection systems, whether they are based on colorimetric or fluorometric spectral changes [35–40]. However, investing this property in fluorescent chemosensors is not always wise and beneficial, since many metals that are less thiophilic than mercury (like silver, cadmium, and lead) can promote reactions similar to those of mercury and thus cause problematic sensing for mercury in relevant environments. In addition, significant challenges still exist in this field, especially those which are related to quenching of fluorescent signals by foreign interference presence. Therefore, optimal ratiometric chemosensors (based on colorimetric spectral changes) for mercuric ions that possess fast response at ambient temperature, can selectively detect

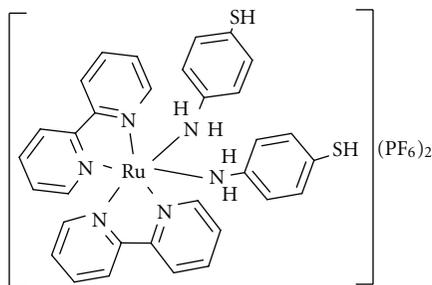


FIGURE 1: Structure of the *Cis-Ruthenium-bis[2,2'-bipyridine]-bis[4-aminothiophenol]-bis[hexafluorophosphate]*, (Ru-4-ASP).

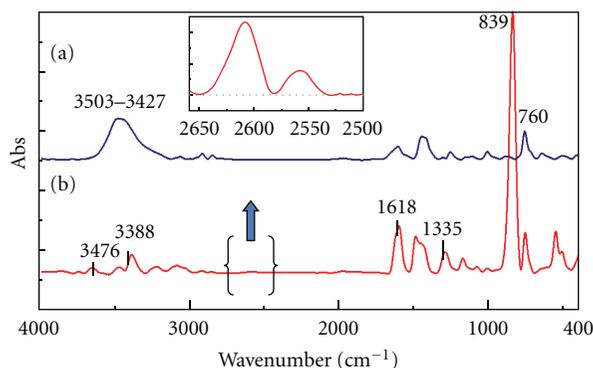


FIGURE 2: IR spectra of (a) $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and (b) The complex Ru-4-ASP. Enlargement of the SH bands in Ru-4-ASP in the frequency range $2500\text{--}2650\text{ cm}^{-1}$ is shown in the inset.

Hg(II) ions, and can operate in aqueous media are still highly demanded.

Polypyridine-Ru(II) complexes are interesting chromophores. The assembly of oligopyridyl groups around Ru(II) center yields mono- or polymetallic complex ions that have been studied extensively for their potential ability as fluorescent chemodetectors [41–43] and energy or electron transformers [44–47]. Furthermore, these Ru(II)-metallo complexes, in some cases, have demonstrated good photo-physical and colorimetric sensing properties. Actually, this feature has attracted our attention, and Ru(II)-bipyridine derivative was employed in this study as a potential carrier for preparation of new optical chemosensors.

In this paper, Ru(II)-bis(bipyridine) was selected to act as the carrier for the sulfur-containing 4-aminothiophenol moiety, which will act as the receptor for obtaining a new chemosensor for mercuric ions. The incorporation of the Hg(II) cations into thiols of the coordinated 4-aminothiophenol ligand would be expected to influence the absorption properties of the Ru(II)-bipyridine core and thus allowing access to a new potential chemosensor based on the chromophore-spacer-receptor concept.

2. Experimental

2.1. General. All reagents were obtained from commercial sources and were used without further purification. Column

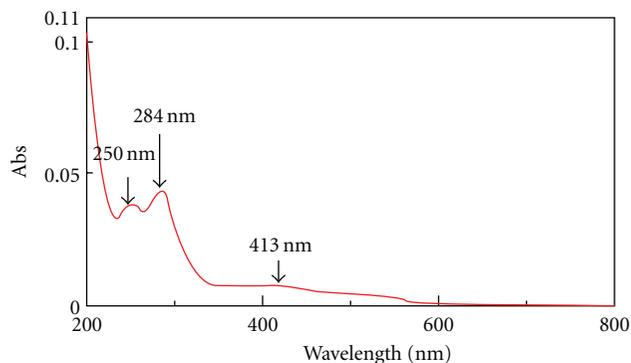


FIGURE 3: UV-vis absorption bands in Ru-4-ASP ($1.0\ \mu\text{M}$) complex.

chromatography was performed with Silica gel 60A/35–70 μm , Merck Al_2O_3 90 basic (0.063–0.200 mm). ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz. The chemical shifts were reported using the residual solvent signal as an indirect reference to TMS: acetone- d_6 2.05 ppm (^1H) and 29.84 ppm (^{13}C). UV/vis spectra were recorded for 50% ethanol/water (v/v) solutions on a Shimadzu UV-1800 spectrophotometer using 1 cm quartz cuvettes. IR measurements were collected on a JASCO FT/IR-4100. All IR spectra were recorded as pressed disks of the sample dispersed in KBr powder. Typically, for each spectrum, 100 scans were coadded at 4 cm^{-1} resolution. Microanalyses (C, H, N, S) were performed using Euro EA elemental analyzer 3000. Conductivity measurements were carried out using JENWAY 4010 conductivity meter employing 0.001 M solutions of Ru-4-ASP complex. Potentiometric titration was carried out using KHP standardized with 0.05 M NaOH solution employing the Russell model RL150 Potentiometer. The pH readings were taken after adding 1 mL of 0.05 M sodium hydroxide increments allowing 30 seconds to pass to ensure complete mixing before each pH measurement.

2.2. Synthesis

2.2.1. *Cis-Ruthenium-bis[2,2'-bipyridine]-dichloride dihydrate, Ru(bpy)₂Cl₂·2H₂O*. It was prepared and characterized as reported, by Sullivan et al. [48]

2.2.2. *Cis-Ruthenium-bis[2,2'-bipyridine]-bis[4-aminothiophenol]-bis[hexafluorophosphate] (Ru-4-ASP)*. Under argon/ N_2 atmosphere, $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.35 g, 0.67 mmol) and 4-aminothiophenol (4-ASP) (0.16 g, 1.4 mmol) were dissolved separately in a 1 : 1 mixture of absolute ethanol/water (v/v). After mixing, the resulting solution was subjected to reflux overnight, after which NH_4PF_6 (2.5 g, 13.5 mmol) dissolved in 2 mL water was added to precipitate the complex. The solid product was collected by filtration and washed thoroughly with 10 mL portions of water followed by diethyl ether. The complex was then dried under reduced pressure to yield 0.36 g (81%), m.p. $205\text{--}207^\circ\text{C}$ (dec.). Found C, 42.76; H, 3.18; N, 9.31; S, 6.21 calc. for $\text{C}_{32}\text{H}_{30}\text{F}_{12}\text{N}_6\text{P}_2\text{RuS}_2$, C,

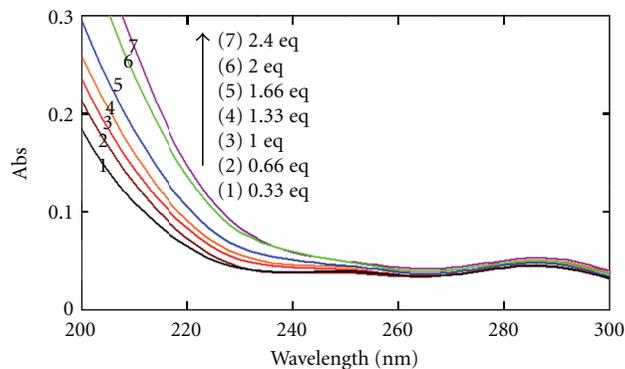


FIGURE 4: The change in 250 nm absorption band of Ru-4-ASP ($1.0 \mu\text{M}$) as a function of the added $1.0 \mu\text{M}$ Hg(II).

40.30; H, 3.17; N, 8.81; S, 6.72. $^1\text{H-NMR}$ 400 MHz (acetone- d_6) δ (ppm) 10.05(dd, $J = 1.6, 5.6$ Hz, 2H, H-6, bpy), 8.55 (dd, $J = 1.2, 7.6$ Hz, 2H, H-3, bpy), 8.47 (dd, $J = 1.6, 6.7$ Hz, 2H, H-3', bpy), 8.05 (dd, $J = 7.9, 8.6$ Hz, 2H, H-4, bpy), 7.95 (dd, $J = 7.9, 8.6$ Hz, 2H, H-4', bpy), 7.76 (dd, $J = 1.6, 5.6$ Hz, 2H, H-6', bpy), 7.56 (dd, $J = 5.0, 6.5$ Hz, 2H, H-5, bpy), 7.40 (dd, $J = 5.0, 6.5$ Hz, 2H, H-5', bpy), 7.25 (dd, $J = 1.3, 8.6$ Hz, 2H, H-3'',5''), 6.80 (dd, $J = 1.3, 9.0$ Hz, 2H, H-2'',6''). $^{13}\text{C-NMR}$ (acetone- d_6) δ (ppm) 158.9, 157.3, 156.6, 155.8, 152.4, 139.3, 139.2, 138.4, 138.0, 137.4, 132.3, 130.6, 128.8, 127.4, 127.3, 127.1, 126.3, 124.5, 124.3, 124.2, 123.9, 122.8; UV-Vis λ_{max} (ϵ) 250 nm (3.2×10^4), 284 nm (3.7×10^4), 413 nm (6.7×10^3).

3. Results and Discussion

3.1. Synthesis of Ru-4-ASP Complex. Interaction of the ruthenium complex, $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, with 4-aminothiophenol (4-ASP) has resulted in Ru-4-ASP complex, (Figure 1). This complex, Ru-4-ASP, appears to be ideal for this application since we anticipated that Ru-4-ASP would interact efficiently with Hg(II) ions through the two thiols. This interaction would facilitate spectral changes as a result of mercury interaction. The Ru-4-ASP complex was prepared in good yield by interacting $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with 4-ASP ligand, using one-step procedure. The formed complex was dark brown-reddish colored and was observed to precipitate as solid material immediately upon the addition of the precipitating agent, ammonium hexafluorophosphate.

The structure of Ru-4-ASP complex depicted in Figure 1 was verified by IR, ^1H , and $^{13}\text{C-NMR}$, elemental analysis, conductivity, and potentiometric titration. Introduction of 4-ASP ligand into $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was evidenced by the appearance of the two IR bands in the range 2560–2625 cm^{-1} . These two bands were assigned for the two SH groups of the attached 4-ASP ligand. Since SH is known as a weak IR absorber [49], the portion 2500–2650 cm^{-1} of the spectrum in Figure 2(b) has been blown up to clearly show the two SH bands (see the inset in Figure 2). The appearance of the NH-stretching vibrations at 3388 and 3476 cm^{-1} in addition to the bending band at

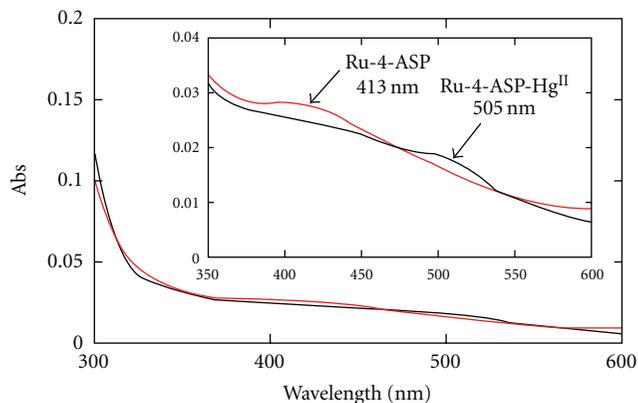


FIGURE 5: The shift in the 413 nm absorption band of Ru-4-ASP ($1.0 \mu\text{M}$) upon addition of ~ 2 equivalents of Hg(II).

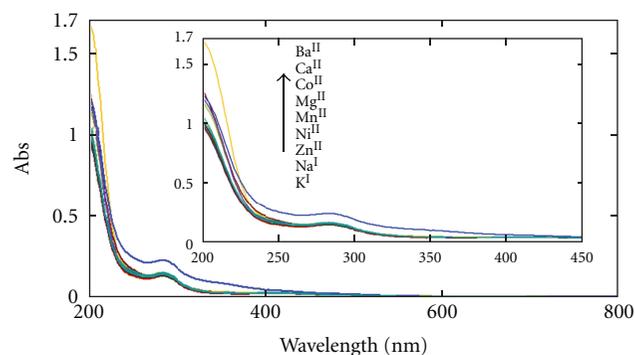


FIGURE 6: Absorption response of Ru-4-ASP ($1.0 \mu\text{M}$) at 250 nm upon the addition of Hg(II) co existed with $1.0 \mu\text{M}$ of Ba(II), Ca(II), Co(II), Mg(II), Mn(II), Ni(II), Zn(II), Na(I), and K(I).

1618 cm^{-1} (Figure 2) indicates the coordination of the $^0\text{1}$ -amino group of 4-ASP to the Ru(II) metal ion. The band at 1335 cm^{-1} , which was consistent with the C-N stretching in $^0\text{1}$ -amine, is another evidence for the coordination of 4-ASP chelate to the $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ moiety via NH_2 group. In 50% water/ethanol (v/v) solution, Ru-4-ASP turned to light brown-reddish-colored solution and gave rise to three absorption bands, two strong bands in the UV-region, at 250 and 284 nm, and a third weak band in the visible region at 413 nm; these bands are shown in Figure 3.

^1H - and $^{13}\text{C-NMR}$, in terms of the peak shift and number of carbon atoms along with the elemental analysis of carbon, hydrogen, nitrogen, and sulfur are consistent with the structure of Ru-4-ASP proposed in Figure 1. On the other hand, the potentiometric titration of one equivalent of Ru-4-ASP with 0.05 M NaOH indicated that thiol groups lost their protons completely in the pH range of 6.0 to 8.8. This range corresponds to two equivalents of sodium hydroxide. Furthermore, the deprotonation intervals of both SH groups were observed to be indistinguishable, where no well-defined sharp equivalence points were noticed; instead, the two regions were overlapped due to the high matching and similarity between the two groups in the Ru-4-ASP structure.

3.2. Interaction of Hg(II) with Ru-4-ASP Dye. A spectroscopic titration of Hg(II) was conducted with $1.0\ \mu\text{M}$ solution of Ru-4-ASP in 50% ethanol/water (v/v) solution at pH 6. Upon addition of an increased amount of Hg(II) ions, the area under the UV-absorption peak corresponding to 250 nm starts to decline, while the band at 284 nm stayed in place without any noticeable change, Figure 4. The reaction responsible for these changes was observed to reach completion within <30 seconds and the observed reduction in the 250 nm absorption band was proportional to the added Hg(II) concentration. Moreover, the saturation of Ru-4-ASP with Hg(II) ions was attained after adding ~ 2.0 equivalents of Hg(II); beyond this point, more additions of Hg(II) brought no spectral changes in the absorption profiles as shown in Figure 4. On the other hand, the visible band at 413 nm was observed to undergo a red shift (into higher wavelength) upon adding two equivalents of Hg(II), Figure 5. At this point, the color of the Ru-4-ASP solution treated with Hg(II) was visually observed, at once, to change from light brown-reddish to orange-reddish. This change in color was not noticed to take place in solution unless the amount of the added Hg(II) reaches the equivalent amount. In a control experiment, Ru-4-ASP was found to retain its original color when treated with only ~ 1.0 equivalent of Hg(II), and this color was found to be stable over time as was observed when the solution was kept on the shelf for more than three weeks.

Similar spectral changes were observed when other salts of mercury, such as mercuric nitrate and mercuric perchlorate, were used. Therefore, it appears that counter anions accompanying Hg(II) ion have negligible effect on the sensation activity of Ru-4-ASP complex. Moreover, the color change in the presence of Hg(II) was found to be insensitive to interferences by other metal cations. That was observed when the Ru-4-ASP complex was allowed to interact with solutions containing submicromolar amounts of Hg(II) and micromolar quantities of the metal cations: Ag(I), Zn(II), Cu(II), Pb(II), Cd(II), Ni(II), Co(II), Fe(II), Fe(III), Mn(II), Mg(II), Ca(II), Ba(II), Li(I), K(I), Na(I), Rh(III), Cr(II), Cr(III). The absorption profiles of some of these ions are shown in Figure 6.

On the other hand, when the optical measurements were repeated for the above cationic solutions but in absence of Hg(II), no change was observed in the three absorption peaks of Ru-4-ASP, Figure 7. However, higher absorbance values were noticed for the 250 nm band when the Ru-4-ASP complex was interacted with Fe(III), Rh(III), and Cr(III). Compared to the divalent ions, the high absorbance values observed with these ions are attributed to the high electron deficiency of the three trivalent ions and consequently the stronger interaction they exhibit with the electron-rich ligand. Fortunately, in all cases, no spectral changes (peak reduction) similar to those witnessed when Ru-4-ASP was interacted with Hg(II) have been induced, Figure 8.

Therefore, the outcomes of the proceeded optical measurements of Ru-4-ASP with Hg(II) demonstrate the lack of interferences by other metal cations or their accompanied anions. This means that Ru-4-ASP complex has a remarkable selectivity toward Hg(II) ion over other metal ions. To see

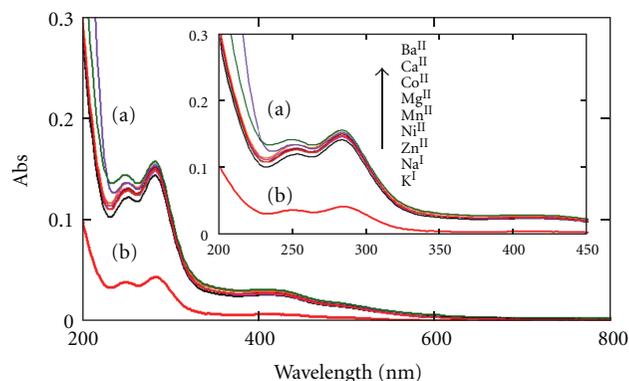


FIGURE 7: Absorption spectra of Ru-4-ASP ($1.0\ \mu\text{M}$) at 250 nm, (a) in the presence of $1.0\ \mu\text{M}$ of Ba(II), Ca(II), Co(II), Mg(II), Mn(II), Ni(II), Zn(II), Na(I), and K(I) and (b) Ru-4-ASP ($1.0\ \mu\text{M}$) with no additions.

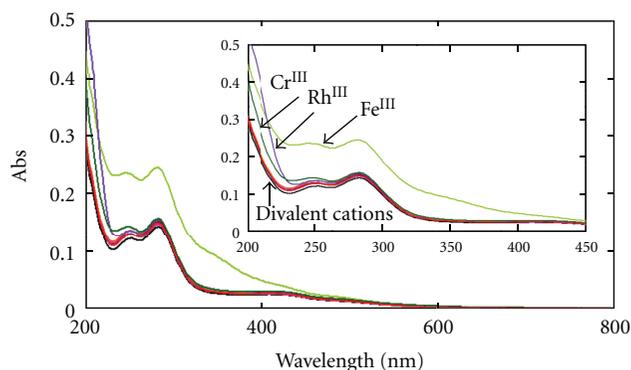


FIGURE 8: The change in absorption response of Ru-4-ASP ($1.0\ \mu\text{M}$) at 250 nm upon the addition of $1.0\ \mu\text{M}$ of trivalent ions: Cr(III), Fe(III), and Rh(III) compared to the divalent ions: Ba(II), Ca(II), Co(II), Mg(II), Mn(II), Ni(II), Zn(II), Na(I), and K(I).

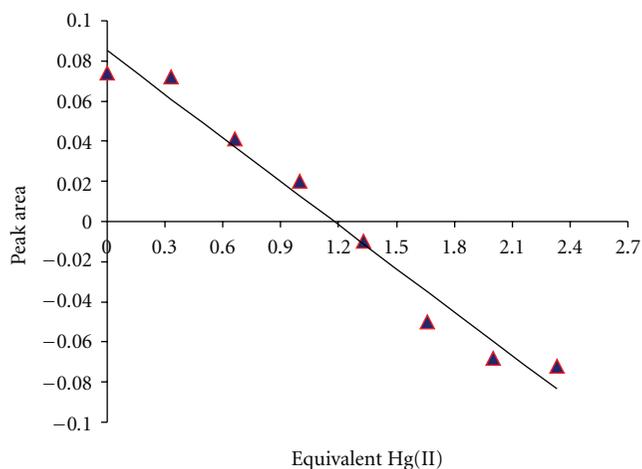


FIGURE 9: Titration of the change in the area of the 250 nm absorption peak of Ru-4-ASP versus equivalents of Hg(II).

the practical applicability of this system as a detector for mercuric ions, the detection limit was evaluated. The titration profile of Ru-4-ASP with Hg(II), which is shown in Figure 9, demonstrates that the detection of Hg(II) is below part per-million level (<0.4 ppm).

In summary, this investigation described in the proceeding has resulted in a development of a highly selective and sensitive Ru-4-ASP-based chemosensor for mercuric ion detection in aqueous medium. This system works efficiently with remarkable high selectivity and sensitivity and under conditions similar to those encountered in relevant Hg(II)-contaminated environments. In such environments, Hg(II) coexists in a matrix of other interfering ions. The findings of this investigation suggest that this strategy would serve as a foundation for practical, rapid detection and precise determination of Hg(II) ions in aqueous environments.

4. Conclusion

The results presented in this investigation demonstrate that, the interaction taking place between Hg(II) ions and Ru-4-ASP complex (through thiol groups) was responsible for the observed spectral changes of the corresponding Ru-4-ASP dye. Interestingly, the investigation described above has resulted in a development of a highly selective and sensitive chemosensor for Hg(II) ions in alcoholic–aqueous solution even in the presence of relatively high concentrations of potentially competing other metal cations. This includes those cations that are identified by the U.S. *Environmental Protection Agency* as potential environmental water pollutants [50] such as Zn(II), Cd(II), Pb(II), Ni(II), and Fe(II). Furthermore, and in terms of sensitivity, the limit of quantification of the system, based on UV-vis spectroscopy measurements, was estimated to be lower than 0.4 ppm, providing a good chemosensation for Hg(II) ions.

Acknowledgments

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