The C$_2$-Symmetry Colorimetric Dye Based on a Thiosemicarbazone Derivative and its Cadmium Complex for Detecting Heavy Metal Cations (Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$) Collectively, in DMF

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Abstract
The field of chemosensing has been experiencing an exponential expansion in recent times, due to increased demands for simpler and user-friendly analytical techniques, in order to combat and confront the challenges of industrial pollutions in the twenty-first century. Metal complex-based chemosensors have received little attention while exhibiting excellent sensing properties, comparing to their organic counterparts. Thus, a thiosemicarbazone-based (H) and its cadmium complex (P) were synthesized, characterized and their photophysical and chemosensing properties were investigated in DMF solvent. The addition of molar equivalents of selected cations (of nitrates or chloride salts) to H and P, produced visually detectable colour changes as well as remarkable spectral shifts. Explicitly, the two probes (H and P) were able to collectively discriminate heavy metal cations such as Cd$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Ag$^+$, both in DMF, among all other heavy metal cations tested. None of the anions could be detected by H or P, even when the tetrabutylammonium salts (TBAs) were used, the action presumably ascribed to the solvent effect. Thus, H and P can be used to selectively and sensitively detect the presence of heavy metal cations, via naked-eye detectable colour changes in an aqueous soluble solvent such as DMF.

Keywords Cadmium-complex sensor · Cd(II) and Ni(II) probe · Thiosemicarbazone sensor

Introduction
The concentration of toxic heavy metals and other chemical species in environmental streams has been on the rise in recent decades, exacerbated by the rapid increase in chemical effluents released from industries and factories. As a result, pollution has become a major issue of concern around the globe due to the accumulation of chemical concentrates in environmental streams [1–3]. The development of simple analytical tools to monitor and control chemical entities in environmental streams and physiological systems is high in the priority list of many research fraternities around the world. Chemosensing has emerged out as an alternative analytical method to detect the presence of chemical entities (cations, anions, or neutral species) in different mediums, based on chemical and geometrical complementarity between the host (sensor) and guest (analyte) [4–7]. In this light, different probes have been proposed and studied in the literature, based on different structural designs and thus sensing mechanisms. The designs of sensors have been largely based on organic molecules, mostly enabled through intramolecular or photoinduced electron/charge transfers [8–13]. However, there is a limited number of metal complex based chemosensors reported, presumably ascribed to the synthesis complexity and the cost involved [14–19].

Metal complexes have been extensively applied in different application throughout the technological revolutions, ranging from pharmaceutical products [20, 21], biological active agents [20, 22–24], solar energy conversion materials [25–27], storage materials [28, 29], catalysis [30–33], and so on, as well-summarized [34]. Metal complex based sensors can be effective sensing probes, due to their excellent chemical stability and photophysical properties. Some of the few known selective and sensitive metal complex based-probes, range from ruthenium, copper, iron, and so on, displaying excellent resoluteness and reproducibility, in discriminating a range of anions such as fluorides, hydroxides, cyanides, and acetates, as well as cations such as mercury, copper, zinc, etc. [14–16, 35–37]. Reports of both colorimetric and fluorometric metal complex based sensors have been published,
facilitated by charge transfer mechanisms due to coordination-induced/chelation-induced, metal-to-ligand, photoinduced, and intramolecular charge transfer process [7, 38–40].

The discrimination of cations in any system is normally facilitated by chelation-induced or coordination-induced charge transfer, through a process of “lock & key” analogy [14, 41–43]. Thus, the interpretation revolves around the thorough understanding of host-guest chemistry, which had generated a huge interest in the field of chemical and biochemical sensing [35, 44–47]. Numerous reports on probes sensitive and selective to cations have been published in recent decades now, however, satisfactory sensing modules that meet the ideal performance standards, in terms of costs, safety and easy-to-produce, remain desirable [35, 48–50]. Furthermore, even though literature is filled with cation sensing probes for copper [51–55], cadmium [43], nickel [56–58], and cobalt [59–62], most of these sensors were metal-free based chemosensors [63–67]. Thus, the interest in metal complex-based sensors is still very high on the priority list, and therefore are still being pursued in many research fraternities.

Consequently, herein, we report a sensing system based on a thiosemicarbazone derivative and its cadmium complex. Most reports on cadmium based studies only focused on the negative impact of its toxicity on the physiological system, very few are reporting on its potential positive aspects [68, 69]. Thus, the study was motivated by the fact that cadmium complexes do exhibit the potential of positive applications in the field of material science. The thiosemicarbazone-based ligand \( H \) and its cadmium complex \( P \) were synthesized (Scheme 1) and their chemosensing properties proved sensitive and selective only to heavy metal cations in DMF, as a solvent of choice.

**Experimental**

**General**

All reagents used were of analytical grade, used as received from the commercial sources unless mentioned. UV-Vis spectroscopy was performed with Perkin Elmer Lambda 35 spectrophotometer in a standard 3.0 ml quartz cuvette with a 1 cm path length. \(^1\)H NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer in DMSO-\( d_6 \). Elemental analyses (C, H, and N) were carried out on a Perkin Elmer 240C analytical instrument. Infrared analysis was recorded on a Perkin Elmer FT-IR Spectrometer (both at the University of Namibia). Elemental analysis (EA) and mass spectroscopy (ESI-MS) were carried out at the University of Cape Town. All the measurements were carried out at ambient temperature.

**Materials**

Commercially available chemicals were used without further purification, and were all of analytical grades. All tetrabutylammonium (TBA\(^+\)) salts (\( F^-\), \( Cl^-\), \( Br^-\), \( I^-\), \( H_2PO_4^-\)), hydrated metal nitrate salts (\( Hg^{2+}\), \( Zn^{2+}\), \( Cu^{2+}\), \( Co^{2+}\), \( Ni^{2+}\), etc.), Thiocarbohydrazide, 2-acetylpyridine, \( CdCl_2 \) and all other chemicals were purchased from Sigma-Aldrich. All UV-Vis titrations were performed in 1.0 \( \times \) 10\(^{-5}\) M solution of \( H \) and \( P \) in DMF, except where it is mentioned otherwise.

**UV/VIS Titration Measurements with Anions and Cations**

All UV-Vis titrations were performed on a Perkin Elmer Lambda 35 spectrophotometer in a standard 3.0 ml quartz cuvette with 1 cm path length at ambient temperature, by first drawing 3 ml of \( H \) or \( P \) (1 \( \times \) 10\(^{-5}\) M) in DMF and measure the absorbance. To this solution (3 ml of \( H \) or \( P \), 1 \( \times \) 10\(^{-5}\) M), molar additions of different anions (\( F^-\), \( OH^-\), \( CN^-\), \( AcO^-\), \( Cl^-\), \( Br^-\), \( I^-\), \( HSO_4^-\) (0.03 M)) as tetrabutylammonium ions (TBA) and cations (\( Fe^{3+}\), \( Ag^+\), \( Mn^{2+}\), \( Cu^{2+}\), \( Co^{2+}\), \( Ni^{2+}\), \( Cd^{2+}\), \( Cr^{3+}\), \( Pb^{2+}\) and \( Hg^{2+}\) (0.03 M)) as nitrates, were titrated, each separately, by 0.1 equivalents intervals, till no changes in spectra. The limit to all was set at 5 equivalents, after noticing that no changes were observed upon the addition of up to 4 equivalents for all anions thereafter.

**Syntheses Procedures**

**Synthesis of \( H \)**

The synthesis of \( H \) was as follows. The ethanolic solution (30 ml) of Thiocarbohydrazide (2.01 g, 18.9 mmol) was drop-wise charged with a solution of 2-acetylpyridine (4.30 mL, 38.4 mmol) while magnetically stirred, and catalyzed with a few drops of acetic acid. The solution mixture was refluxed for up to 3 h before a clear crystalline white precipitate appeared in the solution, on cooling to room temperature. The precipitate was then filtered off and washed several times with ice-cold ethanol. The product was dried in vacuum at room temperature and recrystallized from...
ethanol. Yield 74%. FT-IR: 3590, 3400, 3050–3200, 1500, 1460, 1430, 1230. 
$^1$H NMR (400 MHz, DMSO-d$_6$) δ 2.35 & 3.29 (s, dd, -2CH$_3$), 7.35–8.61 (m, Ar-8H), 9.90 (s, 1H, -NH), 10.99 (s, 1H, -NH), (Fig. S1). Elemental Analysis calcd (%) for C, 57.67; H, 5.16; N, 26.90; Found: C 54.3, H 5.67, N 30.4.

**Synthesis of P**

A solution of CdCl$_2$ (1.17 g, 6.4 mmol) dissolved in water (10.00 mL) was added slowly with stirring to a hot solution of H (1.00 g, 3.2 mmol) in ethanol (35.00 mL). Upon mixing the two solutions, a yellow precipitate was readily formed. The precipitate was recovered by Buchner filtration and washed with distilled water. The product was further re-precipitated from ethanol and washed with water. Yield 60%. ESI-MS (m/z): calcd for C$_{13}$H$_{16}$CdN$_6$S$^-$: 426.02; [M-3H$^+$], found: 429.02. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 2.48 & 3.79 (dd, -2CH$_3$), 7.64–8.70 (m, Ar-8H), 9.58 (s, 1H, -NH) (Fig. S2).

**Results and Discussions**

**Photophysical Property Studies of the Dyes**

**Absorption Properties of H**

The absorption spectrum of H was characterized by an intense peak in the UV-region as well as a low energy band in the visible region (Fig. 1a). Precisely, the spectrum was defined by a high energy and intense band in the UV-region with a maximum at 317 nm, which is normally ascribed to localized π–π* transitions. Generally, the absorption bands at a shorter wavelength are attributed to a localized π–π* transition, a trend associated with organic molecules. In addition, weaker absorption bands were observed in the region stretching from 400 nm to about 600 nm, deep in the visible region, which are normally attributed to the intramolecular charge transfer (ICT). Generally, once the ICT is overlapping within the visible region of the spectrum, it is a good signal for potential dye sensitizers, for solar cell application. The dye (H) is chromatically described by a light yellow colour in the particular solvent (DMF) as indicated (Fig. 1a inset).

**Absorption Properties of P**

Accordingly, the absorption spectrum of P was characterized by three distinctive peaks in DMF, a moderately intense peak at 306 nm, an intense high energy peak at 410 nm, and a weak peak at 536 nm (Fig. 1b). The characteristics of the peaks are as follows, the peak at 306 nm in the UV-region is ascribed to the localized π-π* transitions, the high energy peak at 410 nm is due to intramolecular charge transfer, while a weak band deep in the visible region (536 nm) is due to the metal-to-ligand charger transfer (MLCT). The photoinduced MLCT is normally key to many useful properties of metal complexes, ranging from biological activities, chemosensing, and solar harvesting properties since the charge transfer band is situated in the visible region to near-infrared (NIR). The absorption spectrum was visually defined by an intense yellow colour (Fig. 1b inset), accordingly.

**Chemosensing Property Studies of the Dyes**

**Photophysical Properties of H in Response to Ionic Species**

The molar titration of divalent and trivalent heavy metal cations with H was investigated via absorption titrations in DMF, as well as by naked eye colour change observations. Subsequently, the molar addition of Ni$^{2+}$ (as a Nickel

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![Absorption spectra of (a) H and (b) P in DMF at $1 \times 10^{-5}$ M, room temperature](image-url)
Nitrate) to a thiosemicarbazone derivative H, a high energy π-π* transition band at 317 nm experienced through a hypochromic shift, while the moderate ICT energy band at 437 nm underwent a significant hyperchromic shift (Fig. 2a), attributed to the coordination induced charge transfer between H and Ni^{2+}. The absorption spectral changes observed on the addition of Ni^{2+} to H were concomitant with the naked-eye observable colour changes from light yellow to orange (Fig. 2a inset). The two distinctive species co-existing in one solution system was accompanied by two isosbestic points at 289 nm and 374 nm (Fig. 2a). In addition to Ni^{2+}, the probe was able to discriminate the presence of Cu^{2+}, Co^{2+} and Cd^{2+}, both colorimetrically and spectrally (Fig. 2b, c, and d, respectively). The colour changes could be observed in addition to the spectral shifts, as indicated (Fig. 2 insets) respectively. In both cases, spectral shifts observed, H went through a hypochromic shift at 306 nm upon the addition of the analyte, simultaneously with the hyperchromic shift at 410 nm. The hypochromic shifts are due to the chelation-induced effect upon the interaction of cations with H.

Notingly, the addition of other competitive cations such as Fe^{3+}, Mn^{2+}, Cr^{3+}, Pb^{2+}, and Hg^{2+} was non-responsive, thus no significant noticeable colorimetric (Fig. 3) or spectral changes observed upon their addition to H. Interestingly, H did not show any response to the presence of the anions used (Fig. S3), except for the cyanate (TBA salt) ion, which showed some insignificant response (Fig. S3c), which perhaps may be due to the solvent used, a subject for the next investigation another time.

![Fig. 2](image_url)

**Fig. 2** The absorption titration spectra of H (1 × 10^{-5} M) in DMF, with 5 equiv. of (a) Ni^{2+}, (b) Cu^{2+}, (c) Co^{2+} and (d) Cd^{2+} at room temperature.
Furthermore, the visual impact of other cations towards H is displayed (Fig. 3), with colours ranging from brown-orange (Ni$^{2+}$, Co$^{2+}$, and Cu$^{2+}$) to yellow-orange (Cd$^{2+}$, Ag$^+$, Mn$^{2+}$, and Hg$^{2+}$) colour, which are concomitant with spectral characteristics in the section below. The colorimetric changes displayed by different cations upon interacting with H are due to the coordination-induced charge transfer effects, likely to coordinate through soft atoms (nitrogen atoms) electron donors present in the structural framework of H. The selectivity and sensitivity of H towards cations which led to the formation of adducts (H-Ni, H-Co, H-Hg, H-Cu) are influenced by the solvent used, as well as the geometrical complementarity between the host (H) and the guest (cations). The interaction is steered by the principle of supramolecular chemistry concept of self-assembling molecules, once the conditions are rightly set. Noting other metal cations tested did not induce any significant spectral or colorimetric activities (Fig. S4).

**Photophysical Properties of P in Response to Ionic Species**

In the same manner, the molar absorption properties of P upon interacting with cations and anions were studied via spectrophotometric titrations and naked eye colorimetric observations. The molar addition of cations to P in DMF resulted in significant observable spectral and colorimetric changes, due to chemically induced associations (Fig. 4) with each other. The addition of 5 equiv. of Ni$^{2+}$ to P resulted in the gradual diminishing of the ICT band at 410 nm, concomitantly with the formation of a new coordination-induced charge transfer band in the region of 500 nm (Fig. 4a), a resultant of the gradual formation of a P-Ni complexed state. The spectral changes logged were accompanied by colorimetric activities from yellow to orange, via naked-eye observable colour changes (Fig. 4a inset). The isosbestic point at 437 nm was clearly observed, signifying the co-existence of two distinct species at equilibrium in one system.

Moreover, the addition of other cations to a cadmium complex (P), resulted in more or less similar spectral and colorimetric changes (Figs. 4 & 5) in DMF. The molar titration of Cu$^{2+}$ with P showed similarities with the P-Ni complex, both in spectra and colour, displaying a gradually decreased charge transfer band at 410 nm with molar titration. The peak decrease at 410 nm was simultaneous with the formation of a new band in the region of 500 nm (Fig. 4c), ascribed to the chelation-induced charge transfer band, upon the formation of a reddish-orange P-Cu pedant. The spectra were further characterized by two distinctive isosbestic points at 362 nm and 435 nm, confirming the co-existence of more than one species in equilibrium, in the solution system. The spectral changes observed were accompanied by colorimetric activities, changing from yellow to the reddish-orange colour of P-Cu (Fig. 4c inset). The interaction with two more cations (Co$^{2+}$ and Hg$^{2+}$), resulted in similar spectral changes (Fig. 4b & c) as well as colorimetric changes of brown in colour (Co$^{2+}$) and yellow (Hg$^{2+}$) (Fig. 5) both in DMF. The addition of other cations, as well as all the anions, did not induce any significant spectral change or display any noticeable colour change (Fig. S5).

**Association Constants and Binding**

The binding ability of H towards the cations (Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$) were studied by UV–Vis titration experiments by nonlinear least squares fitting curves. The association constant ($K_{ass}$) was calculated using Benesi–Hildebrand plots from UV-Vis absorption spectral titration according to the equation:

$$A = A_0 + \frac{A_{lim} - A_0}{2C_{H}} \left( C_{H} + C_{G} \right) \left( \frac{1}{K_{ass}} - \frac{C_{H} + C_{G} + 1}{K_{ass}} \right)^{2} - 4C_{H}C_{G}^{2}$$

Where $A$ is the intensity of absorbance; $A_0$ is the intensity of absorbance of the host only; $A_{lim}$ is the maximum intensity of absorbance of host when guest is added; $K_{ass}$ is the affinity constant of host-guest; $C_H$ and $C_G$ are the concentration of the host and guest respectively. The association constants of H toward the four cations are listed in Table 1, determined through the extrapolation of calibration curves (Fig. S6). In addition, the association constants of P towards the four cations (Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Hg$^{2+}$) are displayed (Table 1), obtained through the curvilinear curve of absorption responses vs the concentrations of cations (Fig. S7). In both probes, the association constant ranges in the order of $10^4$ to $10^5$ in the ligand and complex, respectively (Table 1). It clearly demonstrates that the association affinity was more stronger in H compared to P, perhaps ascribed to the tetratadentate nature of H, in a 1:1 interaction ration.
Likewise, detection limit (LOD) of all cations by H was calculated using the formula, LOD = 3σ/m, based on the proposed 1:1 interaction ratio. Where σ the standard deviation and m is the slope obtained in the plot of optical response vs. concentration of cations (Fig. S6). The detection limit value implies that H can easily detect cations at micro molar level in DMF. Furthermore, the interaction ratio of P with cations is ambiguous, which could possibly be in a 1:1 or 1:2 (M^{2+}:P), as most of the cations are capable of forming either tetrahedral (Co^{2+}, Cu^{2+}, Hg^{2+} and Cd^{2+}) or square...

![Fig. 4](image_url)  
**Fig. 4** The absorption titration spectra of **P** \(1 \times 10^{-5} \text{ M}\) in DMF, with 5 equiv. of (a) Ni^{2+}, (b) Hg^{2+}, (c) Cu^{2+} and (d) Co^{2+} at room temperature

![Fig. 5](image_url)  
**Fig. 5** Visually observable color changes **P** \(1 \times 10^{-5} \text{ M}\) upon interacting with cations in DMF for Ni(II), Co(II), Cu(II) and Hg(II), while the rest with no noticeable changes, at room temperature
planar (Ni\(^{2+}\) and Cu\(^{2+}\)) geometry [70–75]. The LOD of the cations in P is in the nonamolar range (Table 1), determined using the titration data; calibration curves vs concentrations of metal cations (Fig. S7). These LODs nonamolar levels are far lower than those allowable standards.

The Structural Characterization of the Probes

The ESI-MS and \(^1\)H NMR Studies of H and P

The characterization of H was carried-out by the ESI technique (Fig. S8), whereby its spectrum was defined by six prominent peaks. The peaks were assigned to their corresponding m/z ratios, while the molecular ion, \([M]^+\) peak could as well be observed at m/z 312. For instance, the peak at 297 (33.8%) was assigned to [M - CH\(_3\)]\(^+\) fragment, while the peak at 234 corresponds to [M – Py]\(^+\). The peaks were in agreement with the proposed structure of the ligand (H), where resulting fragments were identifiable by molecular weights. Other observed peaks and their corresponding fragments are indicated in the mass spectrum of H (Fig. 6a), which are summarized accordingly, in the table (Fig. 6b).

Contrastingly, the ESI spectrum of P was characterized by a couple of peaks, which are all in agreement with the predicted structure of the complex (Fig. S9). The spectrum constituted of eight prominent peaks, which could be assigned accordingly, based on the identifiable fragments, by molecular weights. Generally, the imine group formed from the Schiff base is normally weak and vulnerable to breaking, upon exposure to high temperatures during the electrospray ionization process. Thus, fragments fracturing in the vicinity of the imine group of P structure is highly probable and possible. Some of the possible fragmental structures are indicated (Fig. 7), which are corresponding with m/z ratios as well as the molecular ion [M]\(^+\).

The \(^1\)H NMR spectrum of H was characterized by signal peaks ranging from upfield to downfield, due to the underpinning chemical environment of the protons (Fig. S7). Specifically, the spectrum exhibited two distinctly different peaks at 9.5 to 11.5 ppm, ascribed by two –NH protons of H, which are downfield as, expected, due to their proximity to high electronegative species. Another cluster of proton signals in the region of 7 to 9 ppm were assigned to the aromatic protons within the structure of H (Fig. S1), and lastly, another set of peaks with chemical shifts located upfield were assigned to the solvent (DMSO-d\(_6\) at 2.6 ppm) and methyl protons in the structure. The cadmium complex-based, which is diamagnetic in nature due to its 4d\(^{10}\) electronic configuration, was characterized by downfield intense aromatic protons as well as upfield methyl protons as expected. However, comparing the \(^1\)H NMR spectra of P to the original ligand (H) after coordination with Cd\(^{2+}\), it was obvious that the structure experienced major chemical change, which resulted in the downfield shifts.

| Complex* | Stoichiometry | \(K_{ass} (M^{-1})\) | Detection Limit (M) |
|----------|---------------|---------------------|---------------------|
| H-Co     | 1:1           | \(2.50 \times 10^3\) | \(2.5 \times 10^{-10}\) |
| H-Cu     | 1:1           | \(3.33 \times 10^3\) | \(4.0 \times 10^{-10}\) |
| H-Cd     | 1:1           | \(1.14 \times 10^4\) | \(6.0 \times 10^{-9}\) |
| H-Ni     | 1:1           | \(8.70 \times 10^2\) | \(1.00 \times 10^{-10}\) |
| P-Co     |               | \(2.27 \times 10^2\) | \(4.0 \times 10^{-9}\) |
| P-Cu     |               | \(2.56 \times 10^2\) | \(2.40 \times 10^{-9}\) |
| P-Ni     |               | \(1.55 \times 10^2\) | \(1.30 \times 10^{-10}\) |
| P-Hg     |               | \(1.04 \times 10^2\) | \(9.70 \times 10^{-9}\) |

\(\*\) The cations were added in their nitrate salts

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![Fig. 6](https://example.com)  
**Summary of more fragments observed in the mass spectra of H compound**
of the aromatic protons (Fig. S2). The set of –NH protons initially between 9.5 to 11.5 ppm gradually disappeared to almost bareness, ascribed to chelation-induced chemical shifts upon the interaction of H and Cd^{2+} to yield P (H-Cd). Thus, the characterization techniques used to confirm the identity of the structures (H and P) were all closely in agreement with theoretically predicted structures.

**Conclusion**

A thiosemicarbazone-based chemical probe and its corresponding cadmium complex have been investigated and displayed a good potency and efficacy in discriminating the presence of heavy metal cations, including Cd^{2+} and Hg^{2+}, regarded as most toxic. The techniques of using metal complexes as sensors have not been widely explored in literature, comparing to organic-based probes, thus this is one of the additions to the limited body of literature. In addition, the curiosity of using DMF as a choice of solvent has resulted in remarkable observations, that H or P could not sense any of the common anions used, which could have been recognized had a different solvent (MeCN or DMSO) been used. Thus, the solvent effect does play a major role in the recognition of ionic species. This work is generally a very good description of supramolecular chemistry, whereby the self-assembly mechanism takes place in both the ligand (H) and metal complex (P). Despite the fact that P is already in a complex state (Cadmium complex) through coordination bonding with donor atoms (N atoms) achieved by refluxing, secondary interactions through self-assembly and molecular recognition could still be observed via another cation sensing, that has been recognized. Thus, this work contributes significantly towards the developments of chemical probes using metal complex based entities, for heavy metal cation sensing, which are easy and simple to use and apply.

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**Declarations**

**Conflicts of Interest/Competing Interests** There are no conflicts of interest to declare, from all authors.

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