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A New Macrocyclic Ligand-Based Sensor for Nickel(II) Ions

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A new 14-membered macrocyclic ligand containing nitrogen donor atoms was prepared and characterized. The macrocycle behaves as a selective chelating ion exchanger for some metal ions. The PVC-based membrane electrode of the macrocycle shows a Nernstian response for nickel(II) ions over a wide concentration range (0.294 to 58.69×10^2 mg dm^{-3}) between pH 3.0 to 7.0. The electrode is found to possess adequate stability and specific selectivity with a response time of 10 s. The sensor can also be used in a partially nonaqueous medium having a 35% (v/v) nonaqueous content. The membrane exhibits excellent selectivity for nickel(II) ions, and no disturbance is observed by normal interferents like Cu^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, and Hg^{2+} ions. The electrode has been successfully used for estimating Ni^{2+} ions in milk powders, chocolates, and hydrogenated vegetable oils. Small amounts ($\leq5.0\times10^{-5}$ mol dm^{-3}) of hexadecyltrimethylammonium bromide do not disturb the functioning of the membrane sensor.

The first membrane sensor for nickel(II) was developed by Pungor and co-workers[1] using a Ni-dimethylglyoxime complex. Later on, heterogeneous membranes of nickel(II) phosphate[2] in paraffin and silicon rubber, bis(2-ethylhexyl)hydrogenphosphate[3] in PVC and a nickel complex of 1,4,8,11-tetraazacyclotetradecane[4] in araldite were used for preparing electrodes for this metal ion. In addition to these solid-membrane ISEs, liquid-membrane electrodes for nickel using an *O*,*O*′-diisobutyldithiophosphatonickel(II) complex[5] in chlorobenzene, tetradecylphosphonium Ni (II) ion pair[6] in chloroform and dichloroethane, bis(tetraethylammonium), bis(dithiobenzophenazine) nickelate[7] in nitrobenzene and nickel diethyldithiocarbamate[8] in chloroform have also been investigated. These electrodes show poor selectivity and reproducibility and exhibit a non-Nernstian response. Therefore, better electrodes are still to be developed for this ion. For this purpose suitable macrocycles can be used. A macrocyclic class of compounds is found to possess specific selectivity for some metal ions, thereby playing an important role in the separation process. The most important requirement for a macrocycle to act as a good electroactive material in membranes is its ability to act as a selective extractant or to form strong complexes, preferentially with only few metal ions. In this paper, we report on the electroanalytical applicability of a new macrocyclic ligand, 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene membrane, as a nickel-ion sensor. The proposed sensor has a much better selectivity for nickel ions in comparison to the one already reported in the literature. The sensor can also be used in a partially nonaqueous medium using water–methanol and water–ethanol mixtures, and has also been used successfully for estimating the nickel concentrations in milk powders, chocolates, and hydrogenated vegetable oils.

Experimental

Reagents. All chemicals used were analytical - grade reagents and all solutions were prepared in double-distilled water. Chocolates and hydrogenated vegetable oil samples were obtained from the local market. Ash aid solution was prepared by dissolving 20 g of Ca $(NO_3)_2$ and 40 g of Al $(NO_3)_3$ in 100 ml of double-distilled water.

Synthesis and Characterization of the Ligand. The ligand was prepared by reported methods.[9—11] To a stirred solution of ethylenediamine (0.05 mol) in 10 ml methanol, a methanolic solution of acetylacetone (0.05 mol) was added dropwise. The resulting solution was refluxed for 5 h and then concentrated to half of the volume and set aside for 2 d. A cream-colored precipitate, that formed, was collected by filtration through a sintered crucible, washed with methanol and dried under vacuum over P_4O_{10}. The melting point of the compound was found to be 140 °C.

The characteristic bands for the ligand appeared around 1570—1520 cm^{-1} in addition to the C=N[12,13] absorption peak at 1610 cm^{-1} in the IR spectra. The appearance of this band coupled with the absence of a C=O band at ca. 1700 cm^{-1} provides conclusive evidence of the condensation of amine with ketone.

The observed absorption bands in the visible and ultraviolet regions were also recorded (not given in the manuscript) and the spectral behavior is consistent with the square-planar coordination[14] of the compound.

The ^{1}H NMR spectra of the ligand gave singlets at 1.64—2.12 ppm and 4.88—5.32 ppm, attributable to CH_3 (12H) protons and the methylene protons (4H) of the acetylacetone moiety, respectively. A singlet observed at 2.88—3.32 ppm is assigned to the methylene protons (8H) adjacent to the nitrogen.

The observed elemental analysis of the compound confirms well the theoretical one obtained on the basis of the following structure (Chart 1). Found: C, 67.72; H, 9.58; N, 22.52%. Calcd for $C_{14}H_{24}N_4$: C, 67.74; H, 9.67; N, 22.58%.

Electrode Preparation. A heterogeneous membrane of the macrocycle was prepared by dissolving the compound and PVC in diluent tetrahydrofuran. Further, a solvent mediator, dioctyl phthalate (plasticizer), was also added to improve the working concentration range, slope and response time of the membrane sensor. The ratio of macrocycle, PVC, and the plasticizer was varied, to find the optimum proportion which provides a sensor showing the

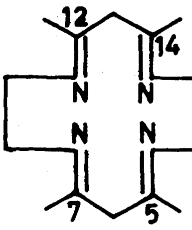

Chart 1.

best performance with regard to the working concentration range, slope and response time. Out of the various recipes tried, membrane No. 4 (Table 1), having macrocycle, PVC, and plasticizer in the ratio 1 : 5 : 2 (w/w), possesses the optimum electroanalytical performance. A solution having the above constituents was stirred well and poured into a casting glass ring resting on a glass plate, and THF was made to evaporate at room temperature. A membrane sheet of about 0.05 mm thick and 6 mm diameter was cut away from the inner edge and glued to one end of a "pyrex" glass tube with Araldite. The process was optimized after a good deal of preliminary investigations so that the membrane generates reproducible potentials and the fabrication of membranes was carefully controlled to have batch-to-batch reproducibility.

Potential Measurements. The membrane was equilibrated in 1.0 mol dm^{-3} ammonium nickel(II) sulfate solution for two days, the optimum time necessary for generating reproducible and stable potentials with low noise when interposed between the test and internal reference solution of 1.0×10^{-1} mol dm^{-3} concentration. The potentials were measured by direct potentiometry[15] at 25±0.1°C with the help of ceramic junction calomel electrodes and a KCl salt bridge. The measurement of the potentials was made from low to high concentrations to avoid memory effects. The ionic strength of various solutions was maintained using NH_4NO_3 (10^{-3} mol dm^{-3}), and pH adjustments were made with dilute acid or hexamine.

Evaluation of Selectivity Coefficient. The potentiometric selectivity of the membrane was evaluated in terms of the selectivity coefficients obtained by a fixed-interference method (as recommended by IUPAC.)

Conductance Measurements. The conductance of the membranes (in different cationic forms) was measured by a modified method adopted by Lakshminarayanaiah and Subrahmanyam,[16] which makes use of a mercury pool on both sides of the membrane to minimize the polarization at the membrane interface. The membrane was cemented between two Pt electrodes with the ligand, and kept in contact with electrolyte solution of 0.1 mol dm^{-3} concentration. The solution was then replaced by mercury previously equilibrated with an electrolyte solution of the same concentration, and the conductance was measured by connecting the platinum electrodes to a conductance bridge.

Sample Preparation and Estimation of Ni^{2+}. The Dry Ashing Method[17] was used for preparing samples for a nickel estimation.

Twenty grams of the samples of hydrogenated vegetable oils (HVO), chocolates, and milk powder each were taken in a silica crucible and 5 ml of ash aid solution was added to it. The mixture was then heated overnight at 400—450 °C in a muffle furnace. The ash obtained was dissolved in 5 ml 0.1 M HNO_3 and 1 ml 0.1 M HCl (1 M = 1 mol dm^{-3}). It was digested on a hot plate until the organic residue was completely oxidized. The solution was finally made up to 50 ml, after filtering it through filter paper, and used for the estimation of Ni^{2+} by Atomic Absorption Spectrometer (Perkin–Elmer AAS ICP 6500) and also by the sensor developed for the purpose after adjusting the pH of the sample.

The reported results are the average of a minimum of two determinations. Blank runs were also carried out and necessary corrections were made if necessary.

Results and Discussion

The response times indicated in Table 1 were evaluated by recording the changes in the potential when a concentration step from 0 to 10^{-6} mol dm^{-3} was made, and calculating the time necessary to reach 90% of the final steady value. The values presented correspond to the mean of several experiments during 2 months, and did not show any alteration during the period considered. The static response time of the proposed membrane i.e. the time in which stable and constant potentials are reported, is almost 10 s over the entire working concentration range, and the potentials stay constant for more than three min, after which a very slow divergence is observed. The standard deviations for twenty identical potential measurements at 10^{-3} mol dm^{-3} concentration of nickel ions (reference solution = 10^{-1} mol dm^{-3}) is ±0.2 mV.

Under laboratory conditions if the membrane is properly stored in distilled water and if cross-contamination is avoided, it can be used for a period of two months without observing any drift in potentials, response time, slope or detection limit; thereafter, a slight change in the slope and response time is observed. This could be corrected by equilibrating the membrane again with 1.0 mol dm^{-3} Ni^{2+} solution of 8 h (lesser time is needed in comparison to the initial equilibration time). With this treatment the assembly could again be used for 2 months and then replaced by a fresh membrane.

Table 1. Optimization of Membrane Ingredients

Membrane No.	Composition in ratio (w/w)			Detection limit	Slope mV per	Response time[b)]
	Ionophore[a)]	Binder	Plasticizer	mol dm^{-3}	decade	s
1	1	7	—	5.0×10^{-5}	23	50
2	1	7	1	5.0×10^{-5}	24	40
3	1	6	1.5	1.0×10^{-5}	25	30
4	1	5	2	5.0×10^{-6}	27	10
5	1	5	1	1.0×10^{-5}	25	30

a) Ionophore = Me_4[14] tetraene N_4. b) Calculated as the time required to attain the 90% of the final steady value for a concentration change from 0 to 10^{-6} mol dm^{-3}.

The potential response of the membrane obtained with pure solutions is illustrated in Fig. 1. It is observed that the membrane electrode can measure nickel ions in the range 0.294 to 58.69×10^2 mg dm^{-3} as per IUPAC recommendation; it also exhibits a Nernstian behavior (slope of 27 mV per decade of concentration).

The pH dependance of the membrane sensor has been tested over the range 1.0 to 9.0 at two concentrations of Ni^{2+} ions viz., 1.0×10^{-2} and 1.0×10^{-3} mol dm^{-3}, and is shown in Fig. 2. pH adjustments in the solutions were made with dil HNO_3 or hexamine. Potentials stay constant from pH 3.0 to 7.0, and the same may be taken as the working pH range of the proposed assembly. Below pH 3.0, a sharp change in potential may be the result of protonation of the macrocycle in the membrane phase, which results in a loss of its complexing ability with metal ions. Above pH 7.0, a change in the potential may be due to interference of OH^- ions in competition with the primary ions.

It has been possible to use the membrane as an indicator electrode for the potentiometric titration of nickel ions. Figure 3 depicts the titration of 20 ml of 1.0×10^{-3} mol dm^{-3} Ni^{2+} ions with a 5.0×10^{-3} mol dm^{-3} EDTA solution. The necessary adjustment of the pH was made before adding the titrant. A perfect stoichiometry is noteworthy in this titration.

It may sometimes be necessary to operate the sensor in a nonaqueous medium as well. As such, the performance of the proposed sensor system was also investigated in partially nonaqueous solvents using water–methanol and water–ethanol mixtures (Fig. 4). The membrane works well in such solvents up to a maximum of 35% (v/v) nonaqueous content without recording any change in the working concentration range as well as the slope. However, with larger nonaqueous contents (> 35%) the slope and working concentration range both decrease appreciably and the potentials become irreproducible. This may be attributed to a change in Henderson as well as interfacial potentials in solutions having a large nonaqueous content.

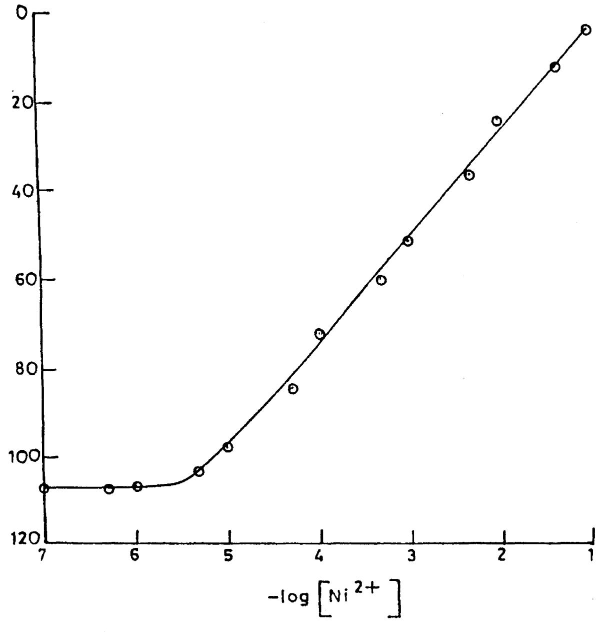

Fig. 1. Plot showing variation of membrane potentials with concentration of nickel(II) ions (taken as ammonium nickel(II) sulfate), for membrane no. 4 under investigation (Table 1).

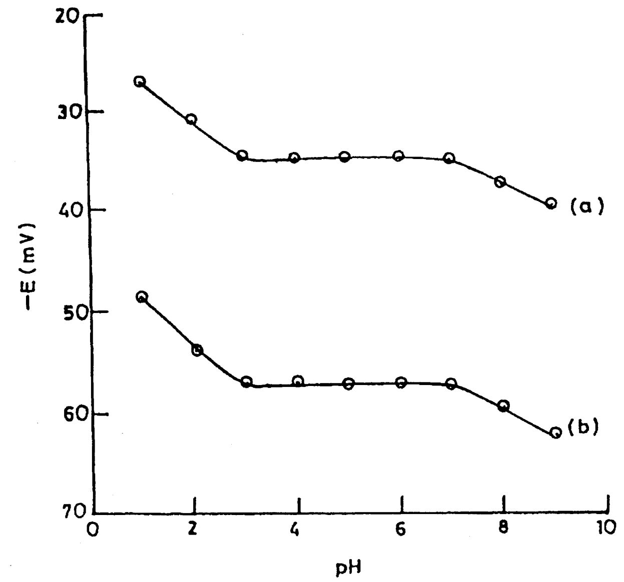

Fig. 2. Plots showing variation of membrane potentials with pH at (1) 1.0×10^{-2} and (b) 1.0×10^{-3} mol dm^{-3}[Ni^{2+}].

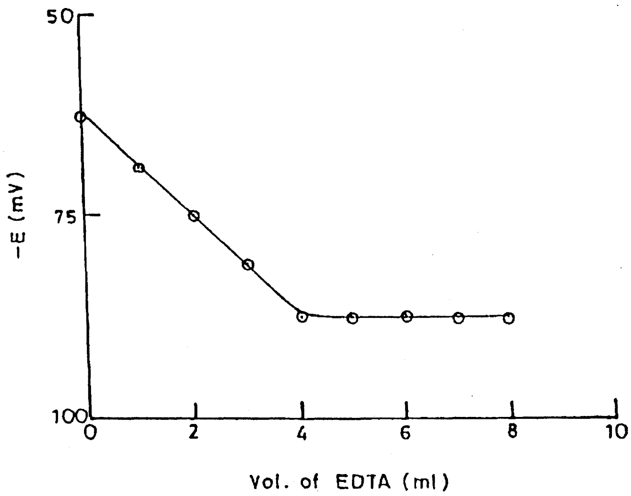

Fig. 3. Titration plot of 20 ml of 1.0×10^{-3} mol dm^{-3} ammonium nickel(II) sulfate with 5.0×10^{-3} mol dm^{-3} EDTA.

The practical utility of the membrane sensor was also observed in solutions contaminated with proteinous matter and washings containing surfactants (Fig. 5), since the effluents from related industries (where the sensor may be used for monitoring Ni^{2+}) may contain some washings as well. Small amounts ($\leq5.0\times10^{-5}$ mol dm^{-3}) of hexadecyltrimethylammonium bromide do not disturb the functioning of the membrane sensor, but at higher concentrations (1.0×10^{-4} mol dm^{-3} and beyond) of which there is slight possibility in actual practice, these can cause some disturbance in the working of electrode assembly.

The performance of the electrode is judged by its selectiv-

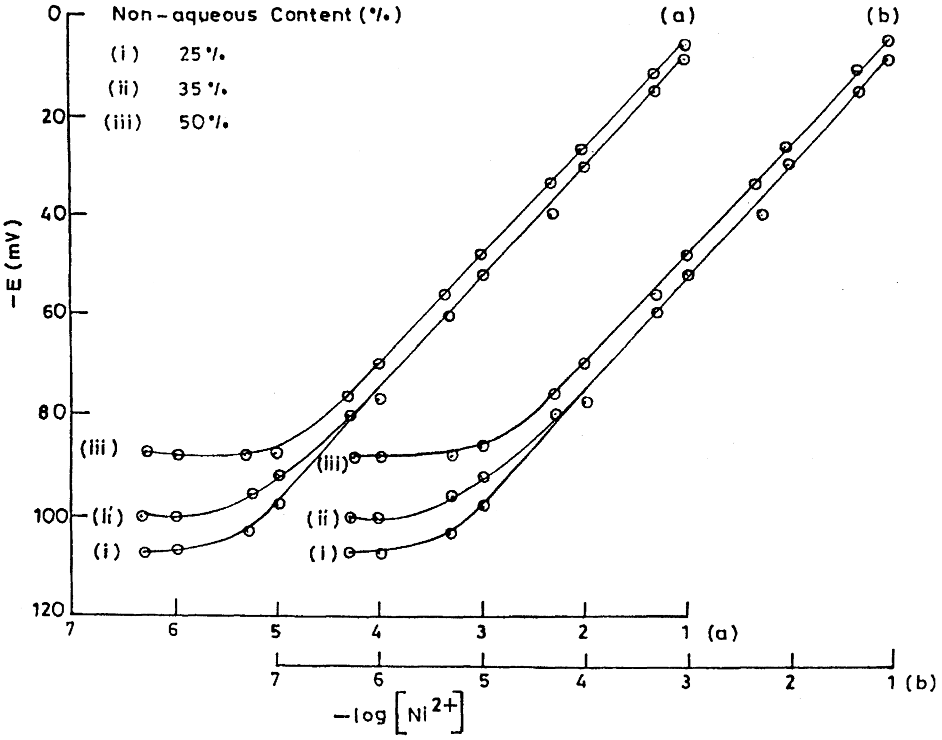

Fig. 4. Plots of potential vs. $-\log [\mathrm{Ni}^{2+}]$ in solvents having nonaqueous content (a) methanol and (b) ethanol.

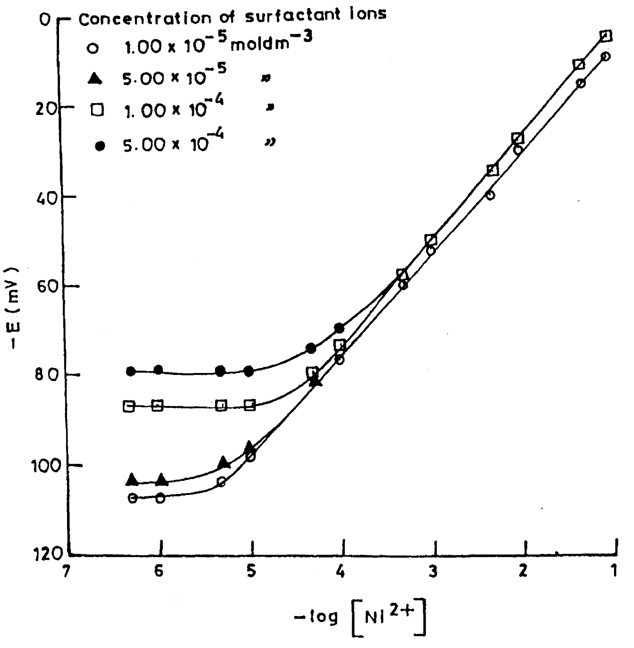

Fig. 5. Plots showing potential vs. $-\log [\mathrm{Ni}^{2+}]$ in presence of various surfactant (Hexadecyltrimethylammonium bromide) ion concentrations.

Table 2. Specific Conductance of PVC-Based Macrocyclic Ligand Membranes in Different Cationic Forms

Cation	Specific conductance 10^2 milli mhos cm^{-1}	Cation	Specific conductance 10^2 milli mhos cm^{-1}
Li^+	3.0	Ni^{2+}	6.8
Na^+	2.8	Mn^{2+}	4.0
K^+	3.0	Zn^{2+}	5.6
Ca^{2+}	3.8	Cd^{2+}	4.0
Sr^{2+}	5.0	Al^{3+}	3.8
Mg^{2+}	5.0	Fe^{3+}	4.6
Pb^{2+}	5.4	Cr^{3+}	4.2

ity for the determinand ion in the presence of foreign ions. Table 2 presents conductance data for a membrane embedded with different cations. The magnitude of the conductance (Table 2) amply justifies its applications as an ion-selective electrode, especially for the estimation of Ni^{2+}. This is assessed by obtaining the selectivity coefficient values, $K^{\mathrm{Pot}}_{\mathrm{A,B}}$ (Table 3 and Fig. 6), by a fixed-interference method (IUPAC), of a number of ions in comparison to nickel at an interference level of 10^{-2} mol dm^{-3}. The membrane exhibits excellent selectivity for nickel ions, and no disturbance is observed by normal interferents like Cu^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, and Hg^{2+}, even at such high concentrations.

The electrode has been successfully used for estimating Ni^{2+} in milk powders, chocolates and edible oils. No other treatment of the sample was necessary, except for the pH adjustment. The results (Table 4) indicate a very good correspondence between the two values (one obtained by AAS and other by the sensor under investigation). The maximum difference observed only in one case is one percent. This indicates the practical utility of the proposed sensor.

It is concluded on the basis of the above studies that a membrane sensor incorporating 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene as the electroactive phase can estimate Ni^{2+} ions in the concentration range 0.294 to 58.69×10^2 ppm. The functional pH range is 3.0 to 7.0, and most of the ions that interfere with Ni^{2+} electrodes do not cause any significant disturbance with this

Table 3. Selectivity Coefficient Values ($K^{\mathrm{Pot}}_{\mathrm{Ni}^{2+},\mathrm{B}}$) of PVC Based Nickel Ion Selective Electrode

Ions	($K^{\mathrm{Pot}}_{\mathrm{Ni}^{2+},\mathrm{B}}$)
Li^+	0.18
K^+	0.15
$\mathrm{NH_4}^+$	0.15
Na^+	0.13
Mg^{2+}	1.49×10^{-2}
Ba^{2+}	1.49×10^{-2}
Hg^{2+}	1.33×10^{-2}
Cu^{2+}	1.12×10^{-2}
Cd^{2+}	1.12×10^{-2}
Zn^{2+}	1.12×10^{-2}
Co^{2+}	1.12×10^{-2}
Ca^{2+}	1.12×10^{-2}
Sr^{2+}	1.12×10^{-2}
Pb^{2+}	9.44×10^{-3}
Cr^{3+}	1.49×10^{-3}
Fe^{3+}	1.33×10^{-3}
Al^{3+}	1.19×10^{-3}

Table 4. Nickel Concentrations in Milk Powder, Chocolates, and Vegetable Oils

Sl. No.	Average nickel concentration as obtained by	
	A. A. S./ppm	Proposed electrode/ppm
1. Milk powder	0.95	0.88±0.02
2. Condensed milk	2.20	2.45±0.14
3. Milk chocolate	0.75	0.72±0.05
4. Chocolate nuts	0.86	0.84±0.01
5. Hydrogenated ground nut oil	0.58	0.56±0.02
6. Hydrogenated vegetable oil	0.85	0.82±0.02

Due to certain technical reasons it has not been possible to mention the make/trade names of milk powder, chocolate, or vegetable oils.

assembly. Its response time is < 10 s, and the sensor can be used for more than three months in aqueous as well as in partially nonaqueous media.

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