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AN EXCELLENT APPROACH TOWARDS THE DESIGNING OF A SCHIFF-BASE TYPE OLIGOCALIX[4]ARENE, SELECTIVE for THE TOXIC METAL IONS

Shahabuddin Memon[a]; Mustafa Yilmaz[a]
[a] Department of Chemistry, Selçuk University, Konya, Turkey

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AN EXCELLENT APPROACH TOWARDS THE DESIGNING OF A SCHIFF-BASE TYPE OLIGOCALIX[4]ARENE, SELECTIVE FOR THE TOXIC METAL IONS

Shahabuddin Memon and Mustafa Yilmaz*

Selçuk University, Department of Chemistry, 42031,
Konya, Turkey

ABSTRACT

A new Schiff-base type oligocalix[4]arene containing two nitrile ligating sites at narrow rim was synthesized via a simple condensation reaction through a wide rim of the calixarene moiety. The extraction ability of the oligomer with selected alkali and transition metals is compared with its monomeric analogous. It has been observed that the oligomer **6** is not selective as compared to its analogae **2** and **3**, but shows a remarkable high affinity towards toxic metal cations such as Cu^{2+}, Hg^{2+} and Pb^{2+}.

Key Words: Calixarene; Copolymer; Schiff base; Phase transfer; Alkali; Transition metal

INTRODUCTION

In recent years, there has been an increased interest in the construction and designing of macromolecules specific for the selective recognition of small species such as cations, anions and neutral molecules. Calix[n]arenes, macrocyclic phenol-formaldehyde oligomers are easily synthesized by "one-pot" procedures. Among them calix[4]arenes have proved to be very useful building blocks for synthetic receptors and enzyme mimics [1–8].

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*Corresponding author. E-mail: myilmaz@selcuk.edu.tr

Based on these properties, specific ligands for analytical chemistry, membranes, decontaminating agents for waste water, dendrimers and star polymers from a calixarene core have been prepared [9–13]. However, the well established binding properties of calix[4]arenes can be enhanced by incorporating them into polymeric skeleton and then be processed into materials suitable for chemical sensor devices such as ion selective elecrodes and filtration/extraction membranes. Early sensor devices based on calixarenes have been prepared by blending technology [14]. The blending methods have several drawbacks including non-uniform ordering of the calixarene units, leaching and difficulty in reproducing a given set of properties in the blend. Therefore, calixarene monomers have been incorporated into polymer backbones utilizing functional groups at the narrow, as well as at the wide rim. The polyacrylates, polyamides, polysiloxanes, carrying calix[4]arene derivatives as side groups linked to the macromolecular chains have also been described [15–23]. Recently, Blanda and Adou have obtained polymers with pendant calixarene systems by copolymerization of monovinyl calixarene derivatives with typical vinyl monomers [24]. Dondoni et al. have successfully copolymerized a calixarene monomer with Bisphenol A to yield a copolymer which exhibited a higher binding affinity for silver ions than the individual calixarene monomer from which it was derived [25]. The scarcity of calixarene-based polymers is in part due to the difficulty in synthesizing rationally designed monomers. Herein, we report the synthesis and binding properties of a calixarene-based copolymer with the following features: (1) the calixarene monomer is in the cone conformation; (2) the site of polymerization is located on the upper rim of the calixarene monomer; (3) the calixarene units are part of the polymer backbone and, (4) the polymer is very selective for Cu^{2+}, Hg^{2+} and Pb^{2+} in two-phase extraction systems.

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis. spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer. Osmometric molecular weight determinations were carried out on a Kanauer vapour pressure osmometer at concentrations of ca. 10^{-3} mol/l in $CHCl_3$.

Analytical TLC were performed on precoated silica gel plates (SiO_2, Merck 60 F_{254}), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. NaH was used as an 80% dispersion in oil and washed twice with n-hexane before use. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4°A. 8–12 mesh). Tetrahydrofuran was dried by refluxing over sodium/benzophenone, then fractionally distilled and stored over molecular sieves (4°A). CH_2Cl_2 was distilled from $CaCl_2$, EtOH was distilled over CaO and stored over molecular sieves (4°A). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy.

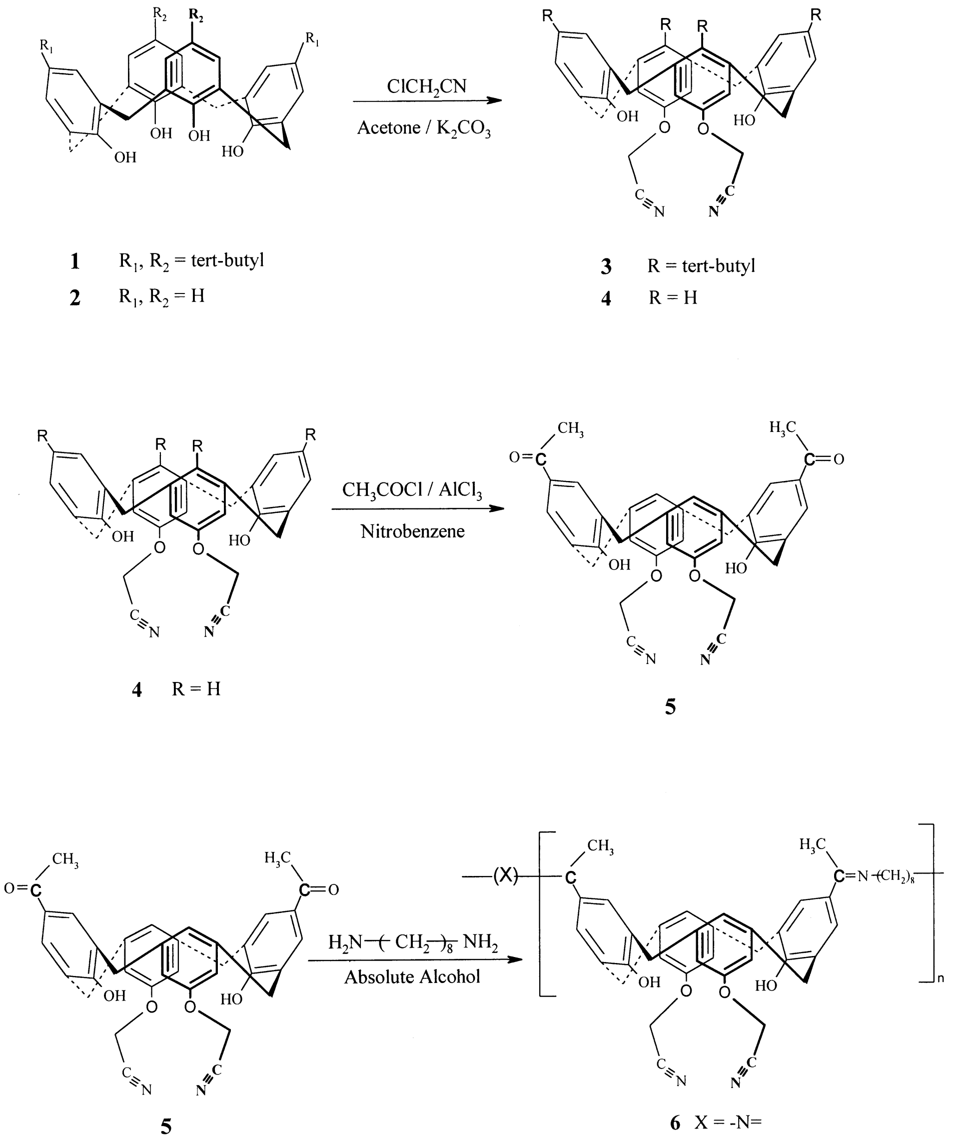
The compounds **1-3** were synthesized according to previously published methods [26, 27, 31]. The syntheses of other new compounds (**4-6**), as illustrated in Scheme 1, have been described as follows:

25,27-Dicyanomethoxy-26,28-dihydroxycalix[4]arene (4)

A mixture of calix[4]arene **2** (2.1 g, 5 mmol) potassium carbonate (2.83 g), chloroacetonitaile (1,3 mL), and sodium iodide (3.2 g) in dry acetone (100 mL), was stirred and heated under reflux for 7 hours. The cooled mixture was filtered through a bed of Celite and the filtrate and acetone washings of the Celite were combined and concentrated to dryness. Recrystellization of the residue from ethanol furnished the dinitrile **3** (1.46 g, 59%), mp. 250°C (decomp.), IR (KBr): 2365 cm^{-1}(CN). ^1H NMR ($CDCl_3$): δ3.40 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$); 4.20 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$); 4.84 (s, 4H, OCH_2CN); 6.80–7.20 (m, 12H, ArH); 7.45 (s, 2H, OH). Anal. Calcd. for $C_{32}H_{26}N_2O_4$; C,76.47; H,5.21; N,5.57. Found: C,76.35; H,5.25; N,5.60.

5,17-Diacetyl-25,27-dicyanomethoxy-26,28-dihydroxycalix[4]arene (4)

Compound **3** (2 mmol) was dissolved in nitrobenzene (150 mL) and anhydrous aluminium chloride (16 mmol) was added, then acetyl chloride (12 mmol) was added dropwise. The mixture was stirred at room temperature for 12 hours, and the reaction was stopped by addition of dilute hydrochloric acid (200 mL). Nitrobenzene was removed by steam distillation. The solid product was dissolved in the chloroform and precipitated in n-hexane. Purified by recrystallization from chloroform-methanol system. Yield: (% 63), mp. 200°C (decom.). IR (KBr): 1760 cm^{-1}(CO), 2360 cm^{-1} (CN). ^1H NMR ($CDCl_3$): δ 2.55 (s, 6H, $COCH_3$); 3.40 (d, J = 13 Hz, 4H, $ArCH_2Ar$); 4.20 (d, J = 13 Hz, 4H, $ArCH_2Ar$); 4.80 (s, 4H, OCH_2CN); 6.95–7.30 (m, 10H, ArH); 8.35 (s, 2H, OH). Anal. Calcd. for $C_{36}H_{30}N_2O_6$; C,73.71; H,5.15; N,4.77. Found: C, 73.65; H, 5.25; N,4.80.



1 R$_1$, R$_2$ = tert-butyl
2 R$_1$, R$_2$ = H

3 R = tert-butyl
4 R = H

4 R = H

5

5

6 X = -N=

Scheme 1.

Synthesis of the Oligomer (5)

Compound **4** (1 mmol) was dissolved in a little amount of THF (~30 mL). To this solution (1:1 equivalent of) 1,8-diaminooctane was added. The reaction mixture was stirred and refluxed for 6 hours under nitrogen atmosphere. The solvent was distilled off and the crude product was washed with ethanol. The solid material was separated, put into the chloroform

(25 mL), the soluble portion was separated by filteration, the clear filtrate was then concentrated to dryness. Finally, purified by reprecipitation from chloroform methanol system. The oligomer **5** was obtained in 48% yield, s.p. 185–187°C. IR (KBr): 1660 cm $^{-1}$ (C=N). ^{1}H NMR ($CDCl_3$): δ 2.50 (bs, 6H, $NCCH_3$); 3.45 (d, J = 13 Hz, 4H, $ArCH_2Ar$); 3.90–4.10 (bs, 20H,CH_2-C, OCH_2CN); 4.40 (d, J = 13 Hz, 4H, $ArCH_2Ar$); 6.90–7.25 (m, 10H, ArH); 7.85 (s, 2H, OH). Anal. Calcd. for $(C_{44}H_{46}N_4O_4)n$; C,76.05; H,6.67; N,8.06. Found: C,76.35; H,6.87; N,8.25.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure [28]. 10 mL of a 2.5×10^{-5} M aqueous picrate solution and 10 mL of 1×10^{-3} M solution of calixarene in $CHCl_3$ were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 minutes, then magnetically stirred in a thermostated water-bath at 25°C for 1 hour, and finally left standing for an additional 30 minutes. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described [29]. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere [30] by the stepwise addition of a 2.5×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 hours. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 hour.

Log-Log Plot Analysis

In order to characterize the extraction ability the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined. If the general extraction equilibrium is assumed to be Eq. (1) with M^{n+} metal ion, L = neutral ligand and with the overlined species referring to species in the organic phase, the overall extraction equilibrium constant is given by Eq. (2). If we introduce the distribution coefficient D, as given in Eq. (3), and taking log of both sides, we obtain Eq. (4).

$$M^{n+}_{(aq)} + nPic^{-}_{(aq)} + x[L]_{(org)} \rightleftharpoons [M(Pic)_n(L)_x]_{(org)} \tag{1}$$

$$K_{ex} = \frac{(M(Pic)_n(L)_x]}{[M^{n+}][Pic^-]^n[L]^x} \qquad (2)$$

$$D = \frac{[M(Pic^-)_n(L)_x]}{[(M^{n+})]} \qquad (3)$$

$$\log D = \log(K_{ex}[Pic^-]^n) + x\log[L] \qquad (4)$$

With these assumptions a plot of the log D vs. log [L] should be linear and its slope should be equal to the number of ligand molecules per cation in the extraction species.

RESULTS AND DISCUSSION

Several aspects of the ionophoric properties of calixarenes and their derivatives toward metal cations were probed experimentally. The objective of the present study was to investigate whether the complexing properties of dinitrile derivative of calix[4]arene could be improved by corporating it into a polymeric backbone through wide rim. Thus, following the strategy outlined in Scheme 1, the monomer, 5,17-diacetyl-25,27-dicyanomethoxy-26,28-dihydroxycalix[4]arene **5**, was derived from the principal starting material 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra-hydroxycalix[4]arene **1** [26]. The conformationally mobile tert-butylcalix[4]arene was first dealkylated at the upper rim [27] to afford **2**, then **1** and **2** were treated with chloroacetonitrile in dry acetone in presence of potassiumcarbonate and sodium iodide as halogen exchanger to yield the compound **3** and **4** [31] which assumed the cone conformation [33, 34]. Generally, the cone conformation is identified in the 1H NMR spectra of calix[4]arenes by the presence of the AX quartet (doublet of doublets) typically at 4.4 and 3.4 ppm for the diastereotopic hydrogens of the methylene carbons connecting the aromatic rings in the calixarene moieties.

In the light of our previous experience [15, 35], the metal binding properties of **3** were investigated and showed high selectivity for Hg^{2+} ions, promoting us to elaborate on its structure so that it could be incorporated into different types of polymers. Thus compound **4** was selectively acetylated on the upper rim by treatment with acetyl chloride in nitrobenzene in the presence of $AlCl_3$ to yield the monomer **5** [32]. The aim was to synthesize lower molecular weight polymer, which may be soluble in most of the organic solvents. Therefore, monomer **5** was transformed to its oligomer without modifying its present design by condensing it with 1:1 equivalent amount of 1, 8 diaminooctane in THF at reflux temperature for 6 hours. During the reaction an sticky mass has been formed. The chloroform soluble portion was taken as the desired polymer. The isolated yield of oligomer **6** was 48%. The conversion of **5** to **6** was infered from the IR spectrum of both compounds. The compound **5** shows a ketonic band at 1760 cm^{-1}, whereas in **6** due to the formation of imide bond this band disappeared and a new band at 1660^{-1} has appeared. The softening point of **6** was determined by using Gallenkamp apparatus and was found that it is decomposed at 185–190°C. The thermal stability of **6** was determined by thermal gravimetric analysis (TGA) in a nitrogen atmosphere. The temperature at which 15% weight loss occurred was 350–400°C. The inherent viscosity for **6** was measured using an Ostwald viscometer with chloroform as the solvent at 25°C and was found to be 0.038. dlg^{-1}. It shows that only oligomeric product was produced. The molecular weight determinations were carried out on a Knaur vapor pressure osmometer at concentrations of ca. 10^{-3} M in $CHCl_3$. The average molecular weight of the oligomer calculated was $M_n = 3300$ g/mole. Thus oligomer contains ca. 4–6 calixarene units in the polymeric skeleton. Even though the signals in the ^1H NMR spectrum for the oligomer was broadened at room temperature, it was possible to discern that the calixarene moieties were still in the cone conformation [33, 34].

Since, from our previous studies [15, 35], it has been noticed that narrow rim functionalized nitrile derivatives of calix[4]arene are very effective extractants for Hg^{2+} ions in two-phase extraction system. In this study our aim was to synthesize conformationally stable forms of the oligomer of the disubstituted calix[4]arene nitrile derivative and compare its binding ability with the corresponding monomer.

Solvent extraction experiments were performed to ascertain the effectiveness of these compounds (**3-6**) in transferring the selected alkali and transition metal cations such as Li^+, Na^+, K^+, Cs^+, Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+} Hg^{2+} and Pb^{2+} from an aqueous to the organic phase. The extraction experimental results are shown in Table 1. As it is clear from the results, compounds **3** and **4** are relatively poor extractants for alkali and transition metal cations used in the extraction experiments except Hg^{2+}; which is in

Table 1. Extraction of Metal Picrates with Ligands[a]

	Pictrate Salt Extracted (%)									
Ligand	Li^+	Na^+	K^+	Cs^+	Cu^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Hg^{2+}	Pb^{2+}
3[b]	< 1.0	< 1.0	< 1.0	< 1.0	2.2	1.8	2.0	3.5	40.0	6.6
4	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	43.2	< 1.0
5	< 1.0	< 1.0	4.72	3.0	< 1.0	6.66	< 1.0	< 1.0	71.58	13.9
6	< 1.0	< 1.0	< 1.0	< 1.0	31.0	11.6	16.0	3.8	82.0	58.0

[a] Aqueous phase, [metal nitrate] $= 1 \times 10^{-2}$ M; [picric acid] $= 2.5 \times 10^{-5}$ M; organic phase, dichloromethane, [ligand] $= 1 \times 10^{-3}$ M; at 25°C, for 1 hour.

[b] Reference: [14].

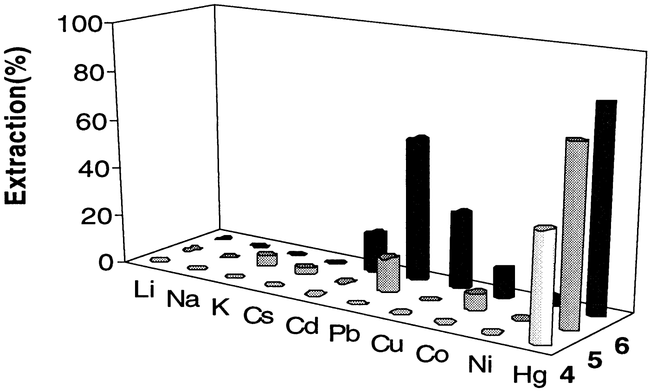


Figure 1. Extraction percentage of the alkali picrates with the compounds at 25°C. $[M^+Pic^-]o = 2{,}5 \times 10^{-5}$ M; $[\text{Ligand}]_o = 1 \times 10^{-3}$ M for **4**, **5** and 1×10^{-3} mole calix[4]-arene unit/gramresin for **6** (water-dichloromethane system).

agreement with our previous studies [15, 35]. Furthermore, it has been noticed that, the tert-butyl groups have no any significant effect on the extraction ability of the compound **3**, because compound **4** also showed similar results in the two phase extraction systems.

The introduction of ketonic groups onto the 1,3 position of the wide rim of compound **4** does not change its over all extraction ability, but only an increase in the Hg^{2+} extraction has been noted (Fig. 1). It is not a surprising result, because Hg^{2+} is a very soft metal ion and has a high affinity towards π-systems (C=O, C≡N).

An interesting result was observed in the case of oligomer **6**, where, due to the presence of Schiff-Base sites in the polymeric backbone shows remarkable change in the extraction of transition metals, especially in the case of Pb^{+2} (58%), Cu^{2+} (31%), and Hg^{2+} (82%). The effectiveness of **6** in transferring transition metals rather than others indicate that, in this case, bridging imide (C=N) groups appeared to be operative and play an important role at water-dichloromethane interphase, since the metal ions could possibly be interacted with these soft ligating sites. It is in agreement with our previous results [36]. The other reason for high binding ability displayed by **6** may be due to the preorganization and fine tuning of the cation binding sites in the lower rim of calixarene moiety, which is immobilized in cone conformation possibly provide such an environment for the complexation of metal cations.

Figure 2 shows plots of log D vs. log [L] of Hg^{2+} extraction by **4** and **5** at their different concentrations. In the case of **5**, a linear relationship between log D vs. −log [L] is observed with the slope of line roughly 0.58, suggesting that **5** forms 1:2 reagent:metal complex with Hg^{2+} according to the following equation.

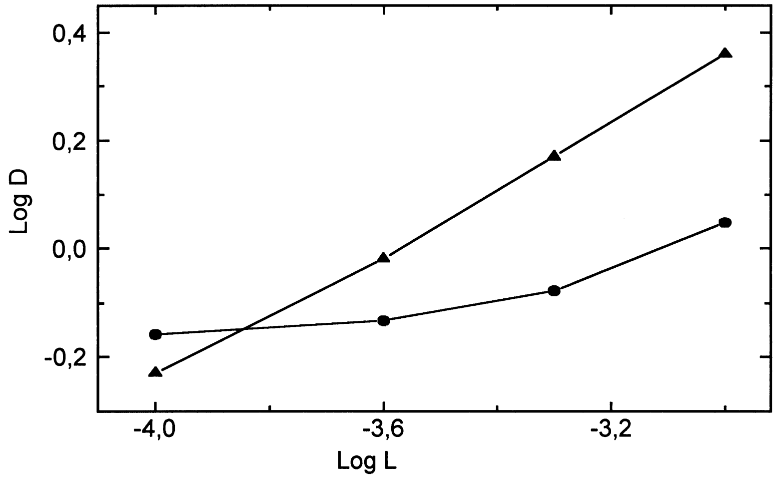


Figure 2. Log D vs. log [L] for the extraction of Hg-picrate by the ligands **4**-(●) and **5**-(▲) from an aqueous into dichloromethane phase at 25°C.

$$2Hg^{2+}{}_{(aq)} + 4\ Pic^{-}{}_{(aq)} + [L]_{(org)} \rightleftharpoons [Hg_2(Pic)_4(L)]_{(org)}$$

The corresponding logoritmic extraction constant (K_{ex}) for compound **5** was found as 3.6. The compound **4** does not show a linear relationship, suggesting the formation of at least two complexes of different stoichometries.

CONCLUSION

In this work, a new Schiff-base type oligomer has been synthesized from calix [4]arene dinitrile derivative (containing diketonic polymerizable reactive sites at its wide rim) and 1,8-diaminooctane through a simple condensation reaction. The thermal stability of the oligomer is up to 320°C and shows a good phase transfer affinity toward toxic metals such as, Cu^{2+}, Hg^{2+}, Pb^{2+}.

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