

Synthesis and metal ion complexation of acyclic Schiff base podands with lipophilic amide and ester end groups

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Abstract A series of acyclic Schiff base podands **14–19** with lipophilic amide and ester end groups were synthesized in good yield and in a simple way. Their transition metal ions complexation was studied using conductometric method in acetonitrile (AN) at 25 °C. Schiff base podands **14–16** showed a continuous decrease in the molar conductances in their complexation with Hg^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} which begins to level off at a mole ratio of 1:1 crown-to-metal indicating the formation of a stable 1:1 complexes. The order of the stability constants of the metal ions studied with the Schiff base podands **14**, **15** and **16** is: $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^+$. Metal ion complexation by acyclic diamide or diester podands involves presumably the oxygen atoms of the carbonyl groups in addition to the nitrogen atoms of the imino groups.

Keywords Acyclic ligands · Schiff base · Podands · Transition metals · Stability constant · Conductivity

Introduction

Podands are a family of noncyclic multidentate ligands such as acyclic ligand **1** (Fig. 1) [1]. They generally form complexes with smaller stability constants than those of corresponding macrocyclic complexes and thus are considered as poor ligands. To enhance their complexing abilities and

their selectivity toward a variety of metal ions, a large number of podands with different end groups and chain lengths were synthesized. Vogtle and Werber reported a variety of podand ligands such as **2** and **3** (Fig. 1) which having quinoline end groups [2]. Some of podands contain ester, amide or pyrone linkages or residues such as **4–9** (Fig. 2) [3–9].

On the other hand, Schiff bases such as **10–13** (Fig. 3) are considered as a very important class of organic component which have a wide applications in many biological aspects [10–13]. These wide applications have generated a great deal of interest in metal complexes. Schiff base-transition metal complexes are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical and analytical fields [13, 14]. The synthesis of Schiff-base acyclic ligands and their solid complexes with transition metal ions were characterized using NMR, MS, X-ray and IR spectroscopy [15–18].

In this report, we have designed and synthesized a new series of podands **14–19** (Fig. 4) by introducing an ester or amide residues as proper ligating groups into the Schiff bases. It is known from calixarene chemistry that the ester and amide groups are one of the most powerful groups introduced into the lower rim of calixarenes in order to enhance their complexing abilities, selectivity and to enhance their solubility in regular organic solvents [19–22].

The complexation properties of podands **14–19** with some of transition metal ions were studied using conductometric technique in AN at 25 °C.

Experimental

Melting points were obtained on electrothermal melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on

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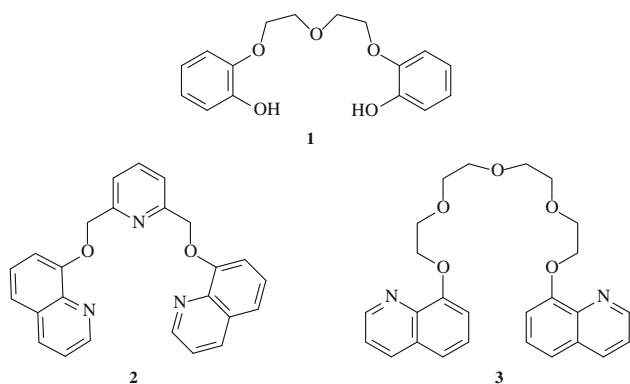


Fig. 1 Structures of podands 1–3

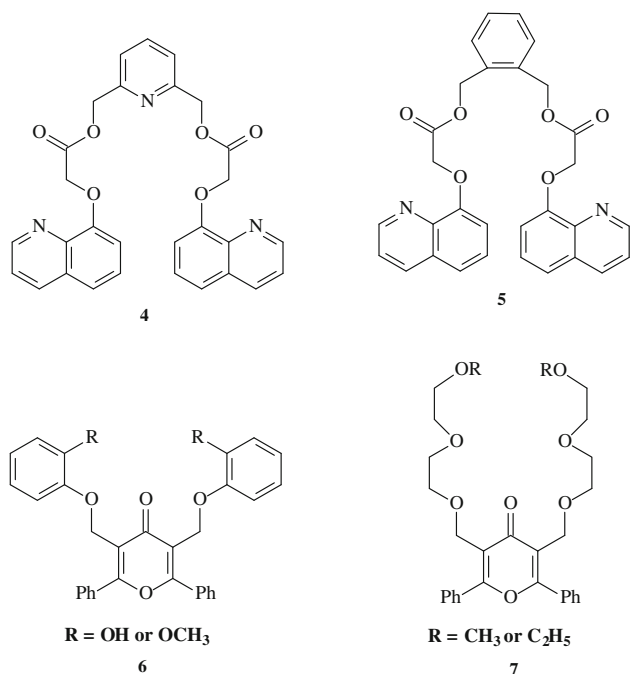


Fig. 2 Structures of podands 4–9

200 and 50 MHz NMR spectrometers, respectively. Unless otherwise noted, samples were dissolved in CDCl_3 . Chemical shifts are reported in ppm relative to TMS used as internal standard. Bruker Avance 400 MHz spectrometer was used for the complexation study. Spectrophotometric

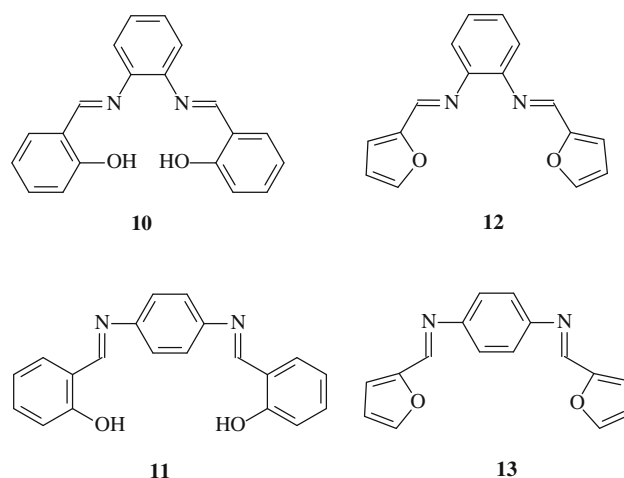
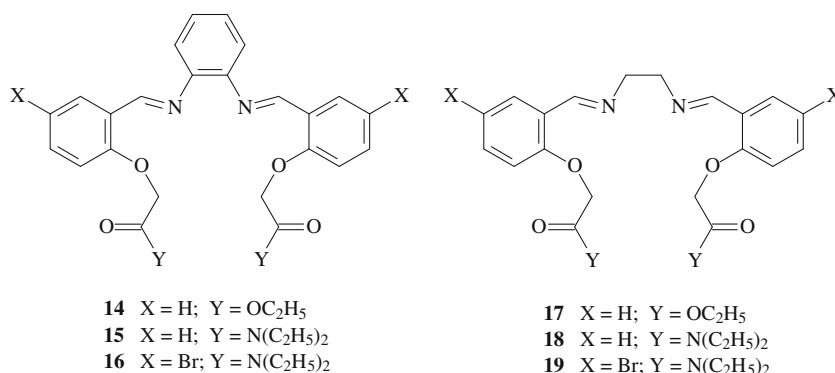


Fig. 3 Structures of podands 10–13

measurements were recorded on Shimadzu UV-2400PC Series. All reagents were of analytical grade and used without further purification. The solvents were used without further purification. The following salts were purchased from the companies indicated: AgNO_3 (Degussa), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Cd}(\text{ClO}_4)_2$ (Aldrich), $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (Aldrich). For the conductivity measurements, acetonitrile was used after fractional distillation. The conductivity of the CH_3CN was less than $1 \times 10^{-7} \text{ S cm}^{-1}$. The description of the conductometer and the details of the conductance measurements have been given previously [23]. Compounds **22**, **26**, **27** were prepared according to the literature procedures [24, 25]. Uv–visible spectrophotometric method was used to construct the Jobs plot. The detailed procedure and the NMR complexation measurements were treated according to the published methods [26–28].

General method for synthesis of Schiff base podands 14–19

Schiff base podands were prepared according to the known method from the condensation of ethylenediamine or 1,2-diaminobenzene with the corresponding aldehyde in a molar ratio of 1:2, respectively, using ethanol as a solvent at reflux temperature [13]. The reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure using rotary evaporator. The product was dried in a desiccator over phosphorous pentoxide. The Schiff bases were obtained in good yields. The ^1H - and ^{13}C -NMR, infrared analysis and elemental analysis measured for the obtained products are consistent very well with the corresponding Schiff base formula.

Fig. 4 Structures of synthesized podands **14–19****Podand 14**

Pale brown semi-solid (79%); FT-IR (KBr, cm⁻¹) 1751 (C=O), 1604 (C=N); ¹H-NMR (CDCl₃): δ 1.28 (t, 6H, *J* = 8 Hz, CH₂CH₃), 4.31 (q, 4H, *J* = 8 Hz, CH₂CH₃), 4.89 (s, 4H, OCH₂CO), 6.96–7.88 (m, 12H, Ar), 8.81 (s, 2H, CH=N); ¹³C-NMR (CDCl₃): 14.3, 61.5, 65.8, 116.9, 117.9, 119.8, 132.7, 133.1, 160.8, 164.2, 167.9. Elemental analysis, found (calcd): H 5.86 (5.78), C 68.47 (68.84), N 5.81 (5.73).

Podand 15

Pale yellow semi-solid (76%); FT-IR (KBr, cm⁻¹) 1682 (C=O), 1601 (C=N); ¹H-NMR (CDCl₃): δ 1.11 (m, 12H, CH₂CH₃), 3.35 (m, 8H, CH₂CH₃), 4.61 (s, 4H, OCH₂CO), 6.89–7.86 (m, 12H, Ar), 8.77 (s, 2H, CH=N); ¹³C-NMR (CDCl₃): 12.7, 13.9, 39.9, 41.2, 61.9, 67.2, 111.9, 120.2, 127.4, 131.7, 141.1, 158.2, 167.3. Elemental analysis, found (calcd): H 7.14 (7.06), C 70.59 (70.83), N 10.11 (10.32).

Podand 16

Brown semi-solid (81%); FT-IR (KBr, cm⁻¹) 1657 (C=O), 1593 (C=N); ¹H-NMR (CDCl₃): δ 1.13 (m, 12H, CH₂CH₃), 3.36 (m, 8H, CH₂CH₃), 4.64 (s, 4H, OCH₂CO), 6.93–7.81 (m, 12H, Ar), 8.79 (s, 2H, CH=N); ¹³C-NMR (CDCl₃): 12.9, 13.8, 40.1, 42.1, 62.2, 67.8, 112.3, 120.6, 127.5, 132.0, 142.0, 159.7, 167.8. Elemental analysis, found (calcd): H 5.24 (5.18), C 54.69 (54.87), N 7.88 (8.0), Br 22.63 (22.81).

Podand 17

Yellow solid (83%); mp 76–78 °C; FT-IR (KBr, cm⁻¹) 1741 (C=O), 1634 (C=N); ¹H-NMR (DMSO-d₆): δ 1.20 (t, 6H, *J* = 7.8 Hz, CH₂CH₃), 3.90 (s, NCH₂CH₂N), 4.21 (q, 4H, *J* = 7.8 Hz, CH₂CH₃), 4.92 (s, 4H, OCH₂CO), 7.0–7.91 (m, 8H, Ar), 8.70 (s, 2H, CH=N); ¹³C-NMR

(CDCl₃): 14.1, 61.0, 62.2, 65.0, 113–132, 157.8, 170.1. Elemental analysis, found (calcd): H 6.35 (6.41), C 66.93 (65.44), N 6.36 (6.48).

Podand 18

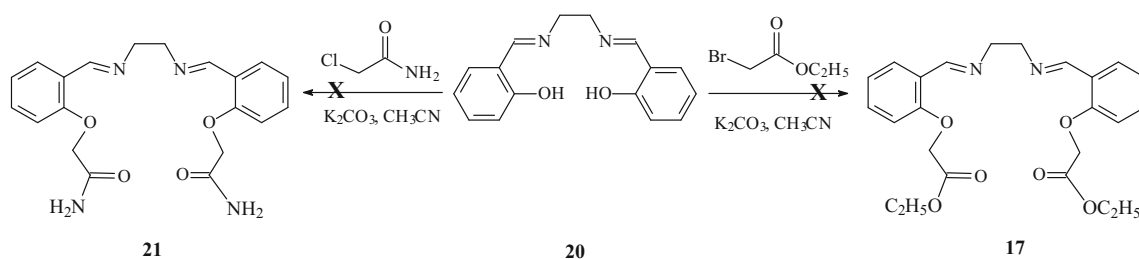
Pale yellow semi-solid (93%); FT-IR (KBr, cm⁻¹) 1652 (C=O), 1601 (C=N); ¹H-NMR (CDCl₃): δ 1.13 (m, 12H, CH₂CH₃), 3.39 (m, 8H, CH₂CH₃), 3.98 (s, 4H, NCH₂CH₂N), 4.69 (s, 4H, OCH₂CO), 6.90 (d, *J* = 3 Hz, 2H), 6.99 (d, 2H), 7.34 (d, 2H), 7.95 (d, 2H), 8.78 (s, 2H, CH=N); ¹³C-NMR (CDCl₃): 12.9, 14.4, 40.4, 41.5, 62.2, 67.9, 112.4, 121.7, 125.1, 127.6, 131.9, 157.5, 158.4, 166.8. Elemental analysis, found (calcd): H 7.59 (7.74), C 67.48 (67.99), N 11.14 (11.33).

Podand 19

Pale brown semi-solid (85%); FT-IR (KBr, cm⁻¹) 1656 (C=O), 1589 (C=N); ¹H-NMR (CDCl₃): δ 1.15 (m, 12H, CH₂CH₃), 3.32 (m, 8H, CH₂CH₃), 3.96 (s, 4H, NCH₂CH₂N), 4.69 (s, 4H, OCH₂CO), 6.77 (d, 2H), 7.40 (d, 2H), 8.06 (s, 2H), 8.67 (s, 2H, CH=N); ¹³C-NMR (CDCl₃): 12.9, 14.5, 40.4, 41.5, 61.8, 67.9, 114.4, 126.8, 130.2, 134.3, 156.6, 157.3, 166.4. Elemental analysis, found (calcd): H 5.34 (5.56), C 51.41 (51.55), N 8.68 (8.59), Br 24.23 (24.49).

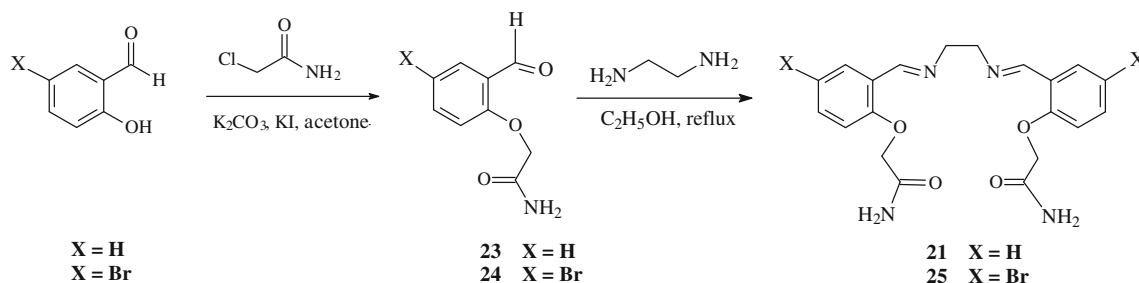
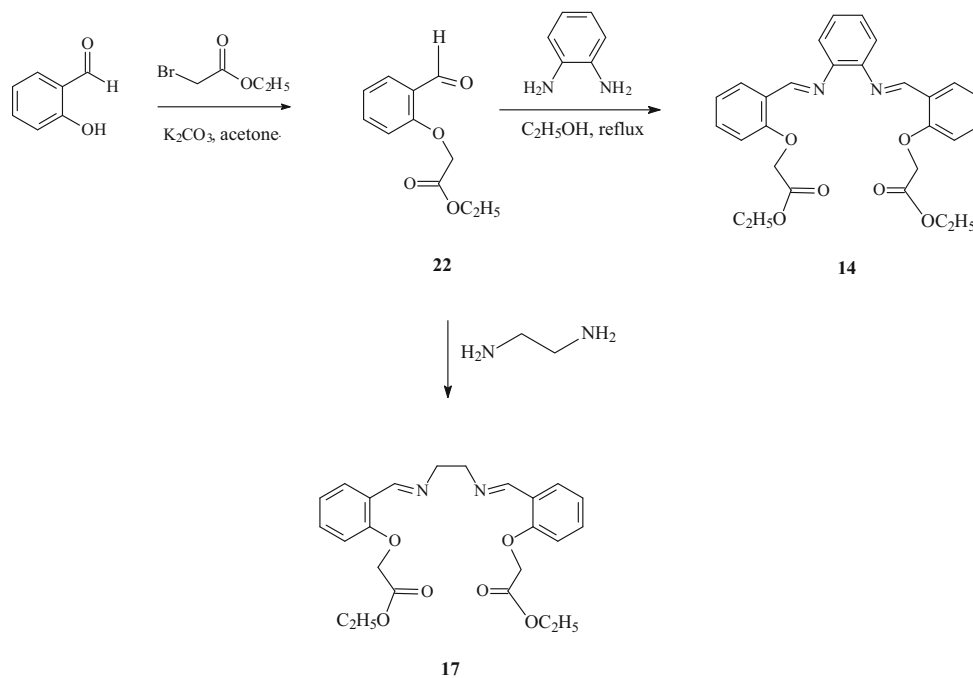
Results and discussion**Synthesis**

The first synthetic approach investigated toward **21** or **17** is outlined in Scheme 1. Diamine **20** was envisioned as being suitable precursor to condense with ethyl bromoacetate or chloroacetamide. However, all attempts at synthesizing **17** or **21** by this route were failed to recover only the starting material **20**. Thus an alternative route (Schemes 2, 3) was applied to prepare Schiff base podands **14**, **17**, **21** and **25**.



Scheme 1 Synthesis of podands **17** and **21**

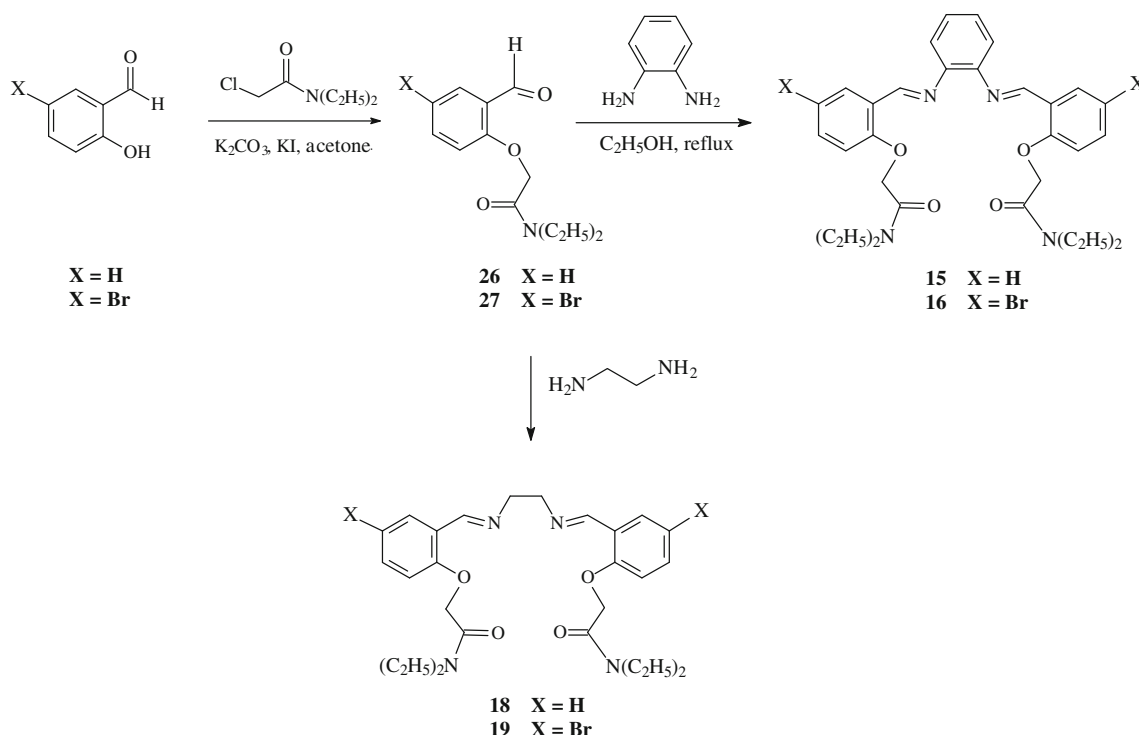
Scheme 2 Synthesis of podands **14** and **17**



Scheme 3 Synthesis of podands **21** and **25**

In this route, salicylaldehyde or 5-bromosalicylaldehyde were condensed with ethyl bromoacetate or chloroacetamide to give the monomers **22**, **23** and **24** in high yield. Treatment of two equivalents of **22** with 1,2-diaminobenzene or 1,2-diaminoethane successfully gave the Schiff base podands **14** and **17** respectively, in high yield. In similar fashion treatment of two equivalents of either **23** or **24** with 1,2-diaminoethane gave both **21** and **25**, respectively. Podands **14** and **17** are soluble in most regular

organic solvents while podands **21** or **25** are only sparingly soluble in DMSO. This poor solubility of **21** and **25** in regular organic solvents such as methanol or acetonitrile causes a limitation in their metal complexation studies. Therefore, in order to enhance their solubility, alkyl groups (ethyl groups) were introduced into the nitrogen atoms of amido groups. This done by reacting of *N,N*-diethylchloroacetamide with either salicylaldehyde or 5-bromosalicylaldehyde to give **26** and **27**, respectively as shown in



Scheme 4 Synthesis of podands **15**, **16**, **18** and **19**

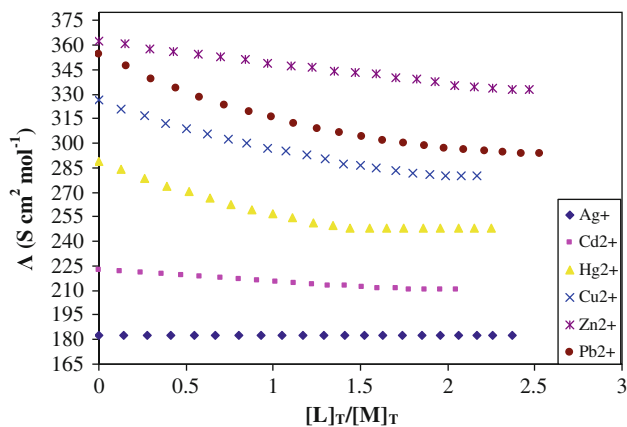


Fig. 5 Molar conductance–mole ratio plots for **14** and metal cations in CH_3CN at 25°C

Scheme 4. Indeed, condensation of two equivalents of **26** or **27** with either 1,2-diaminobenzene or 1,2-diaminoethane gave **15** and **16**; **18** and **19**, respectively which are soluble in most organic solvents.

Complexation studies

In principle, measurements of the variation of electrical conductance with the concentration of metal salts and receptors can determine the strength, stoichiometry and stability constants of complex formation and to assess the

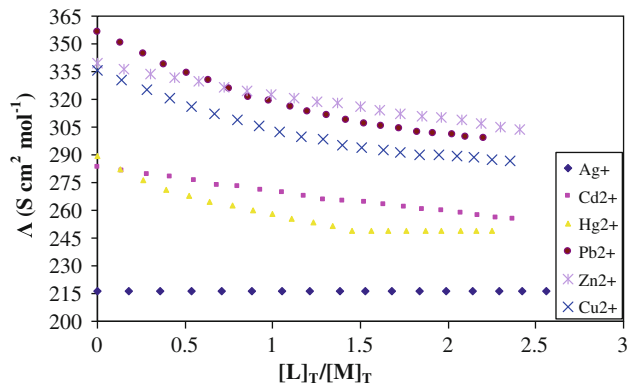


Fig. 6 Molar conductance–mole ratio plots for **15** and metal cations in CH_3CN at 25°C

nature of the interactions taking place. We employed such measurements to establish the stoichiometry of the complexes formed between several individual metal cations and compounds **14–19** and also to determine the stability constants of these complexes. To determine the stability constant in this study, a simplex program, which is specially designed for 1:1 complexes, is applied [29–33]. Complexes other than 1:1 stoichiometry will not fit with this program.

The molar conductance Λ ($\text{S cm}^2 \text{ mol}^{-1}$) of the perchlorate salts of Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , and Hg^{2+} and the nitrate of Ag^+ in acetonitrile was monitored as a function of $[\text{L}]_{\text{T}}/[\text{M}]_{\text{T}}$ at 25°C are given in Figs. 5, 6, 7, 8, 9 and 10.

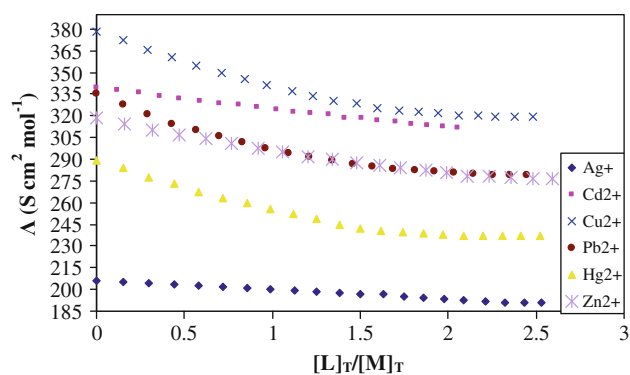


Fig. 7 Molar conductance–mole ratio plots for **16** and metal cations in CH_3CN at 25°C

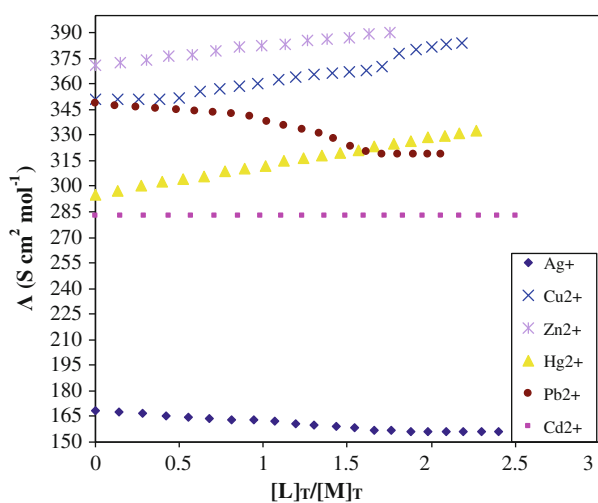


Fig. 8 Molar conductance–mole ratio plots for **17** and metal cations in CH_3CN at 25°C

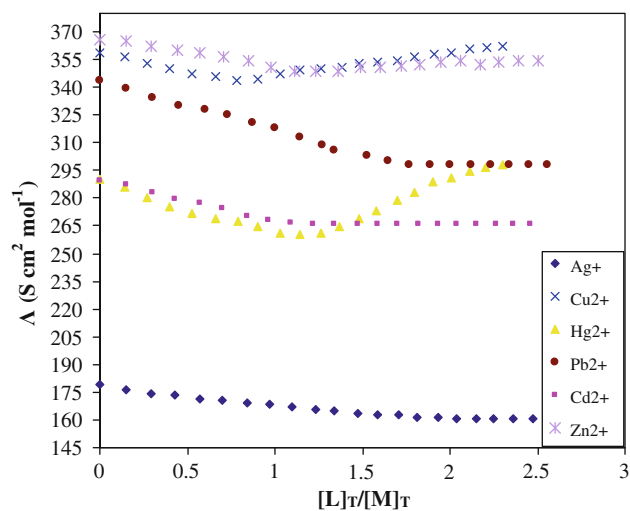


Fig. 9 Molar conductance–mole ratio plots for **18** and metal cations in CH_3CN at 25°C

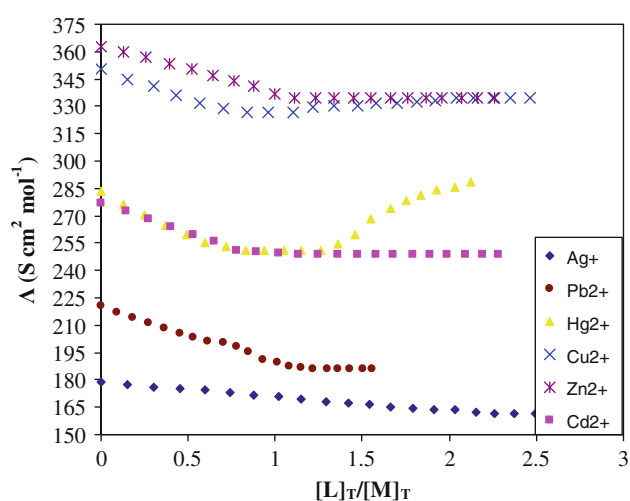


Fig. 10 Molar conductance–mole ratio plots for **19** and metal cations in CH_3CN at 25°C

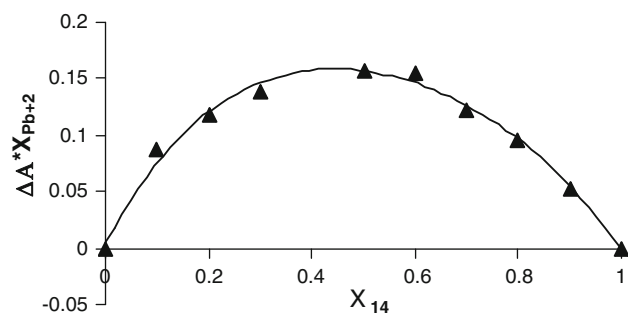


Fig. 11 Job's plot for ligand **14** with Hg^{2+} metal cation in CH_3CN at 25°C

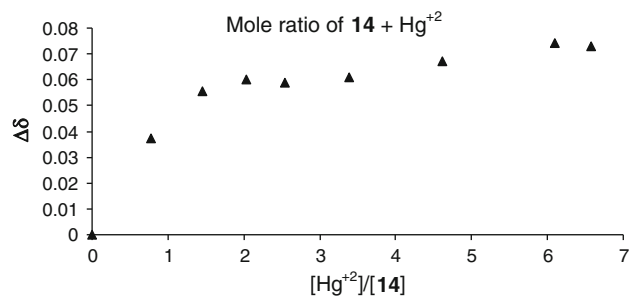


Fig. 12 Plot of chemical shift changes $\Delta\delta$ versus $[\text{Hg}^{2+}]/[\mathbf{14}]$ metal cation for CH_3 protons of the ethyl group of **14** in CD_3CN at 25°C

$[\text{L}]_{\text{T}}$ and $[\text{M}]_{\text{T}}$ are the total concentrations of the ligands **14–19** and of the metal cations, respectively.

It is obvious from Figs. 5, 6 and 7 that the addition of podands **14**, **15**, or **16** (where the bridge is benzene ring) to Hg^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , or Cd^{2+} metal solutions causes a continuous decrease in the molar conductance which

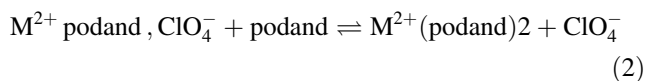
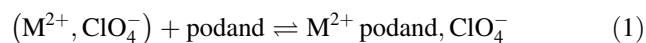
Table 1 log K_{assoc} for complexation of Ag^+ , Cu^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} and Cd^{2+} with podands **14**, **15** and **16** in acetonitrile at 25 °C

Compound	Ag^+	Cu^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}
14	a	3.95 ± 0.10	2.95 ± 0.07	4.24 ± 0.11	4.95 ± 0.13	2.81 ± 0.07
15	a	4.14 ± 0.11	3.29 ± 0.08	4.26 ± 0.12	5.05 ± 0.14	1.83 ± 0.05
16	0.95 ± 0.02	4.24 ± 0.11	3.71 ± 0.10	4.38 ± 0.13	4.43 ± 0.11	2.79 ± 0.07
17	1.67	b (1:2)	1.29	b (2:1)	2.48	a
18	4.10	b	b	b (2:1)	b	5.81
19	3.29	b	5.67	4.52	b	6.33
8	NA	NA	NA	3.72 ± 0.10	NA	NA
9	3.22 ± 0.08	3.16 ± 0.07	NA	3.16 ± 0.07	NA	NA

^a No change in molar conductance was observed

^b The data cannot be fitted in equation

begins to level off at a mole ratio of 1:1 crown-to-metal indicating the formation of a stable 1:1 complexes. This decreasing indicates a lower mobility of the complex than free solvated metal ions. To confirm the 1:1 complexation ratio obtained by conductivity measurements, the complexation between ligand **14** and Hg^{2+} was studied, as an example, using Job's plot (Fig. 11). This figure shows that a maxima of 0.5 is obtained indicating 1:1 ratio. Additional proof for the 1:1 ratio of **14**- Hg^{2+} complex comes also from the mole ratio plot using NMR titration method. Figure 12 shows that the change in δ levels off near the ratio of 1 for CH_3 protons of the ethyl group. Figures 5 and 6 show that no detectable changes in molar conductance occurred upon addition of either a solution of **14** or **15** to Ag^+ solution. This indicates that either no complexation occurred or the mobility of the podand- Ag^+ complex is equal to the mobility of free solvated Ag^+ . An anomalous behavior was observed in the complexation of Hg^{2+} , Cu^{2+} and Zn^{2+} ions with either **18** or **19** (where the bridge is ethylene group). As is obvious from Figs. 9 and 10, addition of either podands **18** or **19** to Hg^{2+} , Cu^{2+} or Zn^{2+} ions causes the molar conductivity to initially decrease until the mole ratio reaches 1:1 and then to increase. Such behavior may be described according to the following equilibria:



It seems that addition of the podand to metal ion solution results in the formation of a relatively stable 1:1 complex (**I**) which is present as an ion-pair. Addition of the second podand to ion-pair complex, causes formation of a stable 1:2 complex with a sandwich structure (**II**) which decreases the interaction of chlorate anion with metal cations and results in dissociation of ion-pair. Similar behavior has been observed by others in their complexation studies of variety of crown ethers with several metal cations [34, 35].

Figure 8 shows that addition of podands **17** to Hg^{2+} , Cu^{2+} or Zn^{2+} metal solutions causes a continuous increase in the molar conductance which does not level off at any ratio. Either podands **17** or **18** form with Pb^{2+} 2:1 (L:M) stable complexes, while podand **19** forms 1:1 complex.

As shown in Table 1, the order of the stability constants of metal cations with **14**, **15**, or **16** is: $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^+$. It is noteworthy that there is no big differences in the stability constants whether the podand ended with alkoxy groups (podand **14**) or ended with diethyl amino group (podands **15**, **16**). This presumably indicates that the metal ion coordinates the oxygen atoms of the carbonyl groups in addition to the nitrogen atoms of the imino groups. This finding was observed also in the complexation studies of transition metal cation with podands **8** and **9** (Fig. 2). It was concluded that the oxygen or sulfur, but not the nitrogen atoms of the end groups participate in metal ion coordination [3].

For comparison purposes, the stability constants of some acyclic ligands **8** or **9** with Cu^{2+} , Ag^+ and Pb^{2+} were incorporated (Table 1). It can be noticed that the stability constants of these acyclic ligands with Cu^{2+} and Pb^{2+} are lower than acyclic Schiff base ligands **14–16**.

Conclusions

Three new acyclic Schiff base ligands **14–19** have been synthesized in a simple way and in a very good yield. These ligands showed good complexation ability for Cu^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} and Cd^{2+} but they showed low selectivity toward metal cations studied. The order of the stability constants of metal cations with the three Schiff base ligands **14–16** is: $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^+$. Schiff base ligands **18** and **19** showed an anomalous behavior in the complexation with Hg^{2+} , Cu^{2+} and Zn^{2+} ions.

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