Journal of Applied Chemical Research, 11, 1, 63-70 (2017)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Antioxidant Activity and Electrochemical Properties of Tetradentate Schiff Bases and Their Cd(II) Complexes

Roya Ranjineh Khojasteh
Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

(Received 14 Jul. 2016; Final version received 18 Sep. 2016)

Abstract

This study describes the effects of the substituents on electrochemical behavior and antioxidant activity of the three tetradentate Schiff bases, containing ethane-1,2- diamine, propane-1,3-diamine and butan-1,4- diamine as the amine part and salicylaldehyde, and corresponding Cd(II) complexes. Cyclic voltammograms of these compounds were recorded in dimethylsulfoxide and 0.1 M sodium perchlorate as supporting electrolyte with glassy carbon as working electrode at different scan rates. The voltammograms of Schiff bases alone showed only one irreversible peak. Voltammograms recorded for complexes showed the presence of quasi-reversible processes taking place at the metal center and reversible process at the ligand part. Both steric and inductive effects of substituents and structure of imine bridge of Schiff base ligands as well as complexes were discussed. These effects appear relevant for the antioxidant activity. Antioxidant activity of the investigated compounds expressed as Trolox equivalent antioxidant capacity is also discussed. The electrochemical behavior showed a high correlation with the antioxidant activity for investigated compounds.

***Key words**: Schiff base-Electrochemical-Complexes- Antioxidant.*

Introduction

In recent years, Schiff bases and Schiff base metal complexes were extensively studied because of their properties such as the ability to reversibly bind oxygen [1, 2], catalytic ability for organic reactions [3, 4], transfer of amino group [5], competing abilities towards some toxic metals [6]. Therefore, these complexes have numerous applications [7], including biological [8–10], clinical [11], analytical [12, 13] and industrial [14]. Examination of the redox properties and defining the redox processes are very important for understanding various forms of biological activity of Schiff

---

* ***Corresponding author:*** *Roya Ranjineh Khojasteh, Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran. Email: r_ranjinehkhojasteh@iau-tnb.ac.ir.*

bases and their complexes [15, 16]. Thus, there has been a strong interest in determination of electrochemical behavior of these compounds and the understanding of the relationship between potentials and the structure as well as activity. Cyclic voltammetry is convenient and widely used method for initial characterization and determination of reactivity of electrochemically active systems such as Schiff bases and their derivates [17, 18].

Furthermore, antioxidants were studied for their capacity to protect organisms and cells from damage induced by oxidative stress. Scientists in various disciplines have become more interested in new compounds, either synthesized or obtained from natural sources that could provide active components to prevent or reduce the impact of oxidative stress on cells [19]. DPPH (2,2′-diphenyl-1-picrylhydrazyl) radical scavenging is one of the important methods to evaluate antioxidant activity which can be determined spectrophotometrically using HPLC but also using a much faster and cheaper methods such as TLC [20]. DPPH is a stable free radical that can accept an electron or hydrogen radical and thus be converted into a stable, diamagnetic molecule.

In this paper, we report the results obtained from the electrochemical studies and TLC-DPPH assay of tetradentate Schiff bases and their Cd(II) complexes in order to evaluate the influence of the substituents on electrochemical behavior and the effect of structures on antioxidative activity of these compounds as well as relation between obtained redox potentials and antioxidant activity.

Experimental

Chemicals

All the chemicals used were of reagent-grade quality. Dimethylsulfoxide (DMSO) was purified further by the standard procedure used before [21]. The supported electrolyte, sodium perchlorate (Merck) was dried before use. 2, 2′-Diphenyl-1-picrylhydrazyl (DPPH) and 6-hydroxyl-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were purchased from Fluka. All of the investigated Schiff bases and their Cd(II) complexes were prepared according to described procedures [22]. The structures of investigated compounds are given in Table 1.

Cyclic voltammetry

The electrochemical experiment was carried out using a CHI760b Electrochemical Workstation potentiostat (CH Instruments, Austin, TX) at room temperature (25 ○C). Cyclic voltammetry was performed using a conventional three-electrode cell (5 mL) equipped with pre-polished glassy carbon as working electrode, a Ag/Ag$^+$ electrode as reference and a platinum wire as an auxiliary electrode. The cyclic voltammograms were recorded in dimethylsulfoxide with 0.1

M sodium perchlorate as the supporting electrolyte. Voltammetric tests were run at a scan rates between 0.05 and 1 V/s. All of solutions (10^{-3} M) were deoxygenated by passing the stream of nitrogen for at least 10 min prior to recording.

Antioxidant activity

Antioxidant activities were determined in vitro by DPPH free radical scavenging assay. Trolox, in concentration range of 0–280 ng/spot, were used as a standard (r = 0.9993). The spots of 1μL of compound solution (0.6 mg/mL) in appropriate solvents were applied by autosampler (Linomat 5, Camag) on RP18 silica plate (Merck, Germany) as well as series of standard solutions in methanol followed by applying of 1 μL of methanolic solution of DPPH (0.15 × 10-3 M) at the same spots. No development was carried out. This plate was left in the dark. After 30 min of incubation plate was scanned. Camag TLC Scanner with CATS evaluation software was used with the following settings: wavelength 515 nm, scanning speed 20 mm/s, multi-level calibration via peak area. The values of antioxidant activity of the compounds are expressed as Trolox equivalent antioxidant capacity (TEAC). Also, the radical scavenging activity (% RSA) was calculated as a percentage of DPPH discoloration using the following equation:

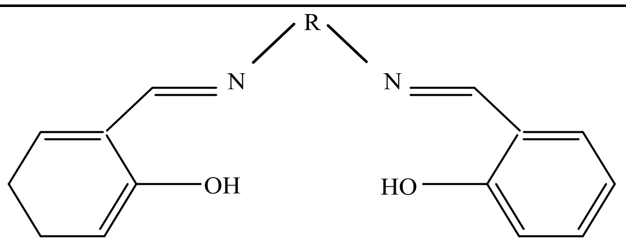
$$\%\ \mathrm{RSA} = \frac{A_{\mathrm{DPPH}} - A_{\mathrm{S}}}{A_{\mathrm{DPPH}}} \times 100$$

where AS is the absorbance of the spots after 30 min of incubation and ADPPH is the absorbance of the DPPH.

Results and discussion

Investigations of the effect of stepwise ligand substitution on electrochemical behavior and antioxidative activity were carried out with three tetradentate Schiff bases (No. 1–3) and three corresponding Cd(II) complexes (No. 4–6) classified into two series depending on the diamine present in the Schiff base (Table 1).

Table 1. Structures of the compounds used in this study.



No	Schiff Base	R	No	Complex
1	H_2Salen	CH_2CH_2	4	[Cd(Salen)]
2	H_2SalProen	$CH_2CH_2CH_2$	5	[Cd(SalProen)]
3	H_2SalButen	$CH_2CH_2CH_2CH_2$	6	[Cd(SalButen)]

Sal: salicylaldehyde, en: ethane-1,2- diamine, Proen: propane-1,3-diamine, Buten: butan-1,4- diamine

Effect of Schiff base substituents

The obtained cyclic voltammograms of Schiff bases clearly indicate that the redox processes of the ligands are highly irreversible. They show the presence of only one anodic peak at potential value in the range from +1.0 to +1.1 V; no cathodic wave occurs in the reverse scan (Table 2). This behavior was observed for a wide range of scan rates from 0.05 to 1 V/s. Hence, such an oxidation process should correspond to a totally irreversible electron transfer. For all Schiff bases under study, this irreversible oxidation peak would be ascribed to the oxidation of the imine group through which these compounds participate in redox processes [23].

Table 2. Potentials of the characteristic peak of Schiff Base.

Schiff Base	**E (V) (vs. Ag/Ag$^+$)**
H_2Salen	+1.080
H_2SalProen	+1.060
H_2SalButen	+1.017

The value of anodic potential varies depending on the substituents present in the compound in accordance with the intramolecular interactions of the imine group. These interactions are changing, as expected, depending on the substituents electronic effect that is present (inductive effect and π-electron interaction) [24]. The effect of anodic potential shift is less pronounced in the substitution of first methyl group in comparison to substitution of both methyls. The introduction of two phenyl groups in the structure of Schiff bases due to the symmetry of the observed compounds has a more pronounced effect on the basicity of the nitrogen atom, which participates in redox processes. Differences in electrochemical behavior are affected not only by the substituents of Schiff bases but also by structure of imine bridge. All of investigated Schiff bases containing propane-1,3-diamine have lower values of potentials comparing to ethane-1,2-diamine. The potentials decrease in following order H_2Salen > H_2SalProen > H_2SalButen. Also, by analyzing the position of peaks obtained at different scan rates may be concluded that the electrochemical processes of ligand are mainly controlled by diffusion. When increasing the scan rates all Schiff bases show a positive peak potential shift, as well as an increase in current intensity. Voltamograms of H_2Salen on different scan rates are shown in Figure 1 as example.

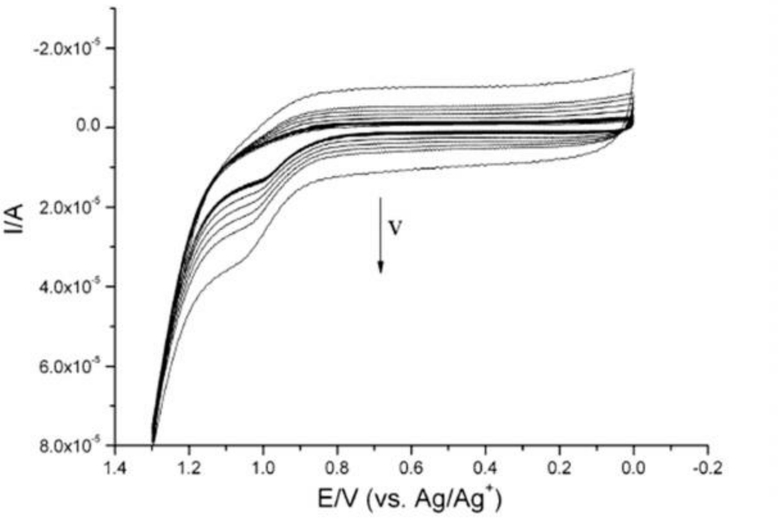


Figure 1. Voltammograms of H_2Salen at different scan rates 0.05-1 V/s.

Effect of substituents in Cd(II) complexes

Knowledge of electrochemical redox processes of the Schiff bases as free ligands is important in properly assigning the electron transfer processes of corresponding Cd(II) complexes. In the voltammograms of investigated Cd(II) complexes (compound 4-6) several characteristic peaks were detected. They are the result of the following redox processes: reduction of liberated Cd(II) to Cd(I) (quasi-reversible), reduction [Cd(II)L to Cd(I)L] and oxidation [Cd(II)L to Cd(III)L] of metal center (quasireversible), irreversible reduction of the imine group and the oxidation of the imine group [24, 25]. Nevertheless, the voltammograms show anodic wave at nearly the same potential as the corresponding peak in the voltammogram of the free ligand. Analysis of the recorded voltammograms of the complexes indicates that the obtained redox potentials depend on the nature of substituents as well as of the structure of the imine bridge. These effects were found in all of the investigated complexes. Figure 2 shows overlapped voltammograms of [Cd(Salen)], [Cd(SalProen)] and [Cd(SalButen)] complexes as example.

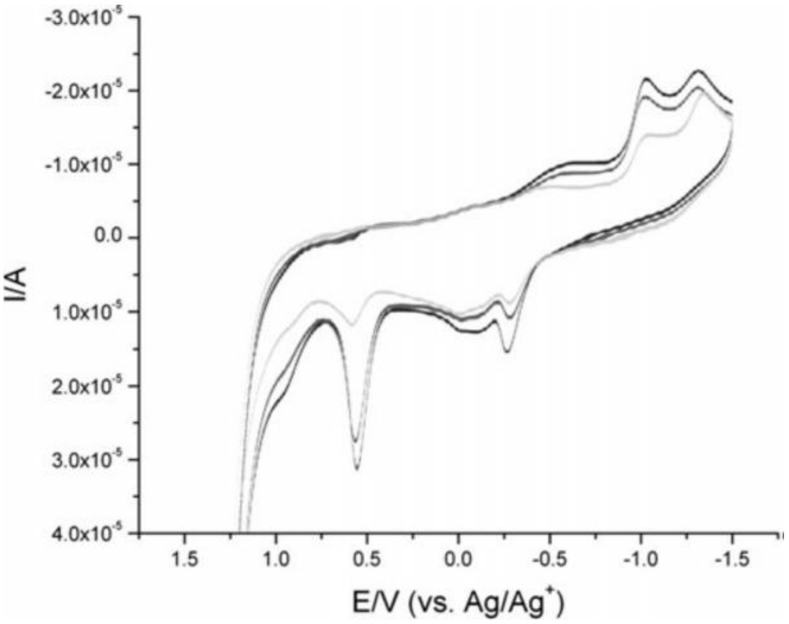


Fig. 2. Overlapped voltammograms of [Cd(Salen)](black), [Cd(SalProen)] (dark gray) and [Cd(SalButen)](gray) at 0.1 V/s

The voltammetric parameters obtained for the Cd(II) complexes are listed in Table 3.

Table 3. Characteristic peaks obtained in voltammograms of Cd(II) complexes.

Compound	E_{c1} (V) (vs. Ag/Ag$^+$)	E_{c2} (V)	E_{a1} (V)	E_{a2} (V)	E_{a3} (V)
4	-1.036	-1.319	-0.270	+0.554	+0.968
5	-1.020	-1.329	-0.284	+0.563	+0.954
6	-1.010	-1.347	-0.290	+0.583	+0.907

Characteristic peak for the reduction of the imine group, which occurs at the potential Ec2 shifts to more negative values with the decrease in the electron-donating ability of the substituents. Also, methyl group may be considered as a π-donor due the hyperconjugation effect of this group [26]. Besides, due to the presence of methyl group in the Schiff base ligands the imine group becomes less resistant to oxidation. It was found that the anodic peak on Ea2 (Table 3) shifts towards more positive values as a result of successive substitution of methyl. The oxidation potential becomes more positive in the sequence of increasing electron-withdrawing effects of the substituents in the ligand. The potentials increase in following order [Cd(Salen)] < [Cd(SalProen)] < [Cd(SalButen)].

Antioxidant activity

The results of antioxidative assay are shown in Table 4. As can be seen from obtained results the investigated complexes (4-6) have greater TEAC values then corresponding ligands (1-3). The results showed that the presence of the Cd(II) ion in the complexes changes the structure of the Schiff base which affects the increase in antioxidant activity of obtained Cd(II) complex. In addition, the substituents in the Schiff bases have a great influence on antioxidant activity. Substitution has effect on TEAC values of ligands and corresponding complexes. The compounds containing propane-1,3-diamine as amine part show lower TEAC values in comparison to corresponding compounds with ethane-1,2 -diamine.

Table 4. Antioxidative activity of the investigated compounds.

Compound	TEAC (mmol/g comp.)	% RSA
1	1.898	36.82
2	1.824	39.28
3	1.388	53.79
4	1.899	38.55
5	1.846	46.15
6	1.618	62.83

It is known that the antioxidant activity is conceivably related to the electrochemical behavior [27]. Increased both the antioxidant activity and the E_a with an increased number of methyl groups for all of investigated Schiff bases were observed. But in the case of Cd(II) complexes a different dependence is noticed; increase of the antioxidant activity and decrease of E_a with an increased number of methyl groups. This is in accordance with rule that complexes with electron-donating groups have lower E_a than compounds with electron-deficient rings and therefore better antioxidant activity (DPPH assay) and higher reducing power [28].

Conclusion

Substituents have a detectable effect on the electrochemical behavior of the Schiff bases and their Cd(II) complexes. Their inductive and steric effects influence the change in electron density on metal ion and basicity of nitrogen. Therefore, there is the difference in electrochemical behavior, which is detected by shifting of anodic and cathodic potentials values strongly influenced by the nature of the Schiff base ligands. Significant correlations have been observed between redox potentials and antioxidant properties. It is found that compounds with strong scavenging capabilities are oxidized at relatively low potentials and therefore the oxidation potentials can be used as a general indicator of radical scavenging ability. Knowledge of the electronic and steric effects that control redox processes of these compounds offers very interesting research opportunities and may be critical in the design of new one.

References

[1] R. Jones, D. Summerville, F. Basolo, *Chem. Rev.*, 79, 139 (1979).

[2] M. Dolaz, V. McKee, S. Urus, N. Demir,

A.E. Sabik, A. Golcu, M. Tumer, *Spectrochim. Acta A*, 76, 174 (2010).

[3] G.H. Oliv, S. Olive, The Chemistry of the Catalyzes Hydrogenation of Carbon Monoxide, Springer, Berlin (1984).

[4] K.S. Alleman, D.G. Peters, *J. Electroanal. Chem.,* 460, 207 (1999).

[5] H. Dugas, C. Penney, Bioorganic Chemistry, Springer, New York (1981).

[6] N. Raman, A. Kulandaisamy, A. Shunmugasundaram, *Transit. Metal Chem*., 26, 131 (2001).

[7] S. Kumar, D. Nath Dhar, P. Saxena, *J. Sci. Ind. Res. India,* 68, 181 (2009).

[8] M. Tumer, D. Ekinci, F.A. Tumer, *Spectrochim. Acta A,* 67, 916 (2007).

[9] K.P. Balasubramanian, K. Parameswari, V. Chinnusamy, R. Prabhakaran, K. Natarajan, *Spectrochim. Acta A*, 65, 678 (2006).

[10] R. Baosic, A. Radojevic, M. Radulovic, S. Miletic, M. Natic, Z. Tesic, *Biomed. Chromatogr*., 22, 379 (2008).

[11] Z.Y. Huang, S.H. Qu, Y. Feng, *Thermochim. Acta*, 320, 121 (1998).

[12] A.K. Jain, R.K. Singh, S. Jain, J. Raisoni, *Transit. Metal Chem*., 33, 243 (2008).

[13] T.R.L. Dadamos, M.F.S. Teixeira, *Electrochim. Acta*, 54, 4552 (2009).

[14] T.L. Yang, W.W. Qin, *Spectrochim. Acta A*, 67, 568 (2007).

[15] L.J. Klein, K.S. Alleman, D.G. Peters, J.A. Karty, J.P. Reilly, *J. Electroanal. Chem*., 481, 24 (2000).

[16] D. Pletcher, H. Thomson, *J. Electroanal. Chem*., 464, 168 (1999).

[17] S. Zolezzi, E. Spodine, A. Decinti, *Polyhedron*, 21, 55 (2002).

[18] S. Ershad, L.-A. Sagathforoush, G. Karimnezhad, S. Kangari, *Int. J. Electrochem. Sci*., 4, 846 (2009).

[19] H.H. Hussain, G. Babic, T. Durst, J. Wright, M. Flueraru, A. Chichirau, L.L. Chepelev, *J. Org. Chem.,* 68, 7023 (2003).

[20] B. Lapornik, A. Golc Wondra, M. Prosek, *J. Planar Chromatogr*., 17, 207 (2004).

[21] D.D. Perrin, W.L.F. Amarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, New York (1988).

[22] R.M. Baosic, Z Lj Tesic, *J. Serb. Chem. Soc*., 60(10), 903 (1995).

[23] M. Ulusoy, H. Karabiyik, R. Kilincarslan, M. Aygun, B. Cetinkaya, S. Garcia Granda, *Struct. Chem*., 19, 749 (2008).

[24] H. H. Monfared, Z. Kalantari, M. -A. Kamyabi, C. Janiak, Z. Anorg, *Allg. Chem*. 633, 1945 (2007).

[25] G. A. Al-Hazmi, M. S. El-Shahawi, A. A. El-Asmy, *Transit. Met. Chem*. 30, 464 (2005).

[26] S. Rayati, A. Ghaemi, N. Sadeghzadeh, *Catal. Commun*., 11, 792 (2010).

[27] A.J. Blasco, M.C. Gonzalez, A. Escarpa, *Anal. Chim. Acta*, 511, 71 (2004).

[28] R. Abreu, S. Falcao, R.C. Calhelha, I.C.F.R. Ferreira, M.R.P. Queiroz, M. Vilas-Boas, *J. Electroanal. Chem*., 628, 43 (2009).