Bulgarian Chemical Communications, Special Edition F, (pp. 33 – 43) 2016

Applications and attributes of nickel (II) schiff base complexes derived of phenylenediamine

A. Sahraei, H. Kargar*, M. Hakimi

Department of Chemistry, Payame Noor University , P.O.BOX 19395-3697, Tehran, I. R. Iran.

Received September 12, 2016; Revised December 26, 2016

The first-row transition metals have been found to constitute a major part of ligands. Nickel that is one of the transition metals has numerous ligands associated with it. The Schiff bases are useful to design coordination compounds with notable structural, magnetic, biomimetic, electrochemical and photophysical properties. This review focuses on Ni^{2+} cation coordination with the Schiff base derivatives of phenylenediamine properties and the most their applications, including Polymerisation, catalytic, Nonlinear optical (NLO), Electrochemical, Magnetic, Photophysicaland antibacterial properties.

Keywords: Schiff base, phenylenediamine, Applications

INTRODUCTION

One of the most important stereochemical models in transition metal coordination chemistry are Schiff base complexes, with ease of preparation and structural variations.One of the Structural characters of a Schiff base is a nitrogen analog of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine [1-2].

Sahraei et al. was synthesized tetradentate N_2O_2 donor Schiff base ligand by adding 6-methoxy-salicylaldehyde to a solution of 4,5-dimethyl-1,2-phenylenediamine in ethanol. This ligand was characterized by ^{1}H NMR, IR and elemental analysis and its solid state structure was determined using single crystal X-ray diffraction [3].

Sahraei et al. have synthesized and determined crystal structure of the nickel (II) complexes by using single crystal X-ray diffraction (Fig. 1) [4].

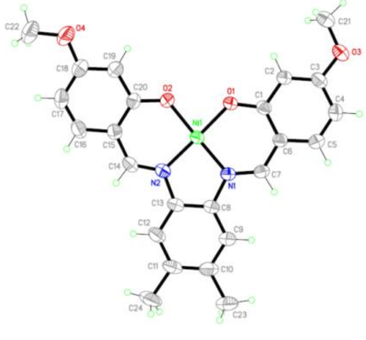
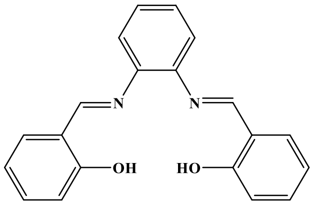


Fig. 1. crystal structure of the nickel (II) complex.

There are a lot of reports on their applications in homogeneous and heterogeneous catalysis in recent years. Schiff base metal complex-catalyzed oxidation of organic compounds is a topic that has been investigated comprehensively many years ago [5-6]. Encapsulation in nanoporous solids such as zeolite is an interesting technique for heterogenization, when the complex is confined exclusively in the zeolite porse, we will not observeany leaching [7].

We determine Schiff base complexes (e.g., salophen 1, Scheme 1) as building blocks of new conjugated polymers and supramolecular structures. A lot of attention has been paid to these molecules as they are known to catalyze oxidation and epoxidation reactions and they have been used highly as luminescent molecules for LED applications [8-9].



Scheme 1. *N*,*N*′-Bis(salicylidene)-1,2-phenylene diamine (salophen).

One of the most famous symmetrical tetradentate ligand is N′-Bis(salicylidene)-1,2-phenylenediamine (salophen), that makes complexes with metal ions and organic compounds [10]. The investigation of complexation reactions of this ligand in nonaqueous matrices can be used as a suitable method to design the analytical systems like, potentiometric sensors [11–13], bulk liquid membrane transport [14], optical sensors [15], solid phase extraction [16] and biochemistry scope [17]. Schiff base complexes have been used as drugs and they possess a wide variety of antimicrobial

---

* To whom all correspondence should be sent:
E-mail: h.kargar@pnu.ac.ir

activities against bacteria, fungi and specific type of tumors. Some medicinesprevent from the growth of tumors when administrated as metal chelated [18].

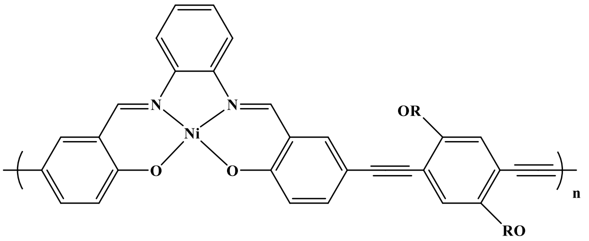
POLYMERISATION PROPERTIES

Polymers including transition metals in the backbone are been a topic for intensive researches sincethese polymers gives properties which are different from their separate organic and inorganic components [19]. Recent researches show that metal-containing polymers may be applicable as catalysts, sensors, and ceramic precursors [20-22].

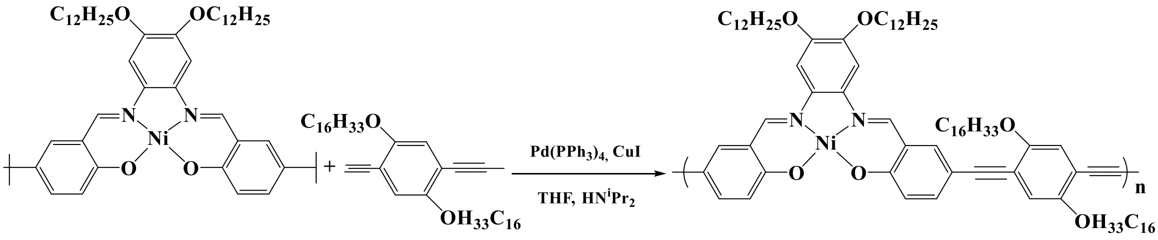
A series of Schiff base Polymers 1-2 were prepared and characterized (Schemes 2-3) the first examples of soluble poly(salphenyl-eneethynylene)s. polymers 1 can be soluble in THF as our work in this field has revealed that rigid, metal-containing polymers are difficult to dissolve. The synthesis of polymers 1 was repeated based on the methodin a published paper the through Pd(0)-catalyzed Sonogashira cross-coupling of bromo- or iodosalphen complexes with 1,4-dialkoxy-2,5-diethynylbenzene [23]. On the other hand, the polymers were insoluble in THF. Actually, when we turned the substituents from octyl in **a** to hexadecyl in **b**, the obtained polymers were almost insoluble in THF. It is probable that luminescence which was reported in this paper is due to the existence of the oligomres or remaining dibromosalphen complex. Despite the supplementary alkoxy substituents polymers 2 were very soluble in THF and they were still insoluble in other solvents such as chloroform and toluene. By multiple precipitations from THF into methanol and acetone the polymers were purified. This polymer is amorphous that shows only an amorphous halo centered at 20° 2Θ.

Preliminary investigations of these polymers show that they are not a suitable candidates for LED applications, but they have been useful for modern chemical sensors or assembling into nanogrids and other supramolecular structures [24].

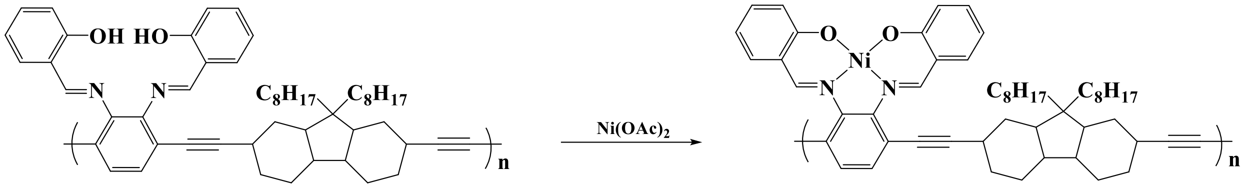
New π-conjugated poly(aryleneethynylene)s polymers including of salophen (Poly-1) and Ni-salophen (Poly-1-Ni) units were achieved in high yields by Pd-catalyzed polycondensation. Poly-1 reacted to Ni^{2+} to give a 1:1 Ni complex quantitatively (Scheme 4). Both the Ni-free and Ni-containing polymers were electrochemically active in the reduction and oxidation areas, and CV (cyclic volammetry) scans of the polymers indicated a reduction peak of the salophene unit at about -2.2 V vs Ag^+/Ag and an oxidation peak of the salophene unit at about 0.8 V vs Ag^+/Ag. π-Conjugated polymers with immobilized salophen-metal complexes will expand the domain of polymerchemistry and coordination chemistry [25].



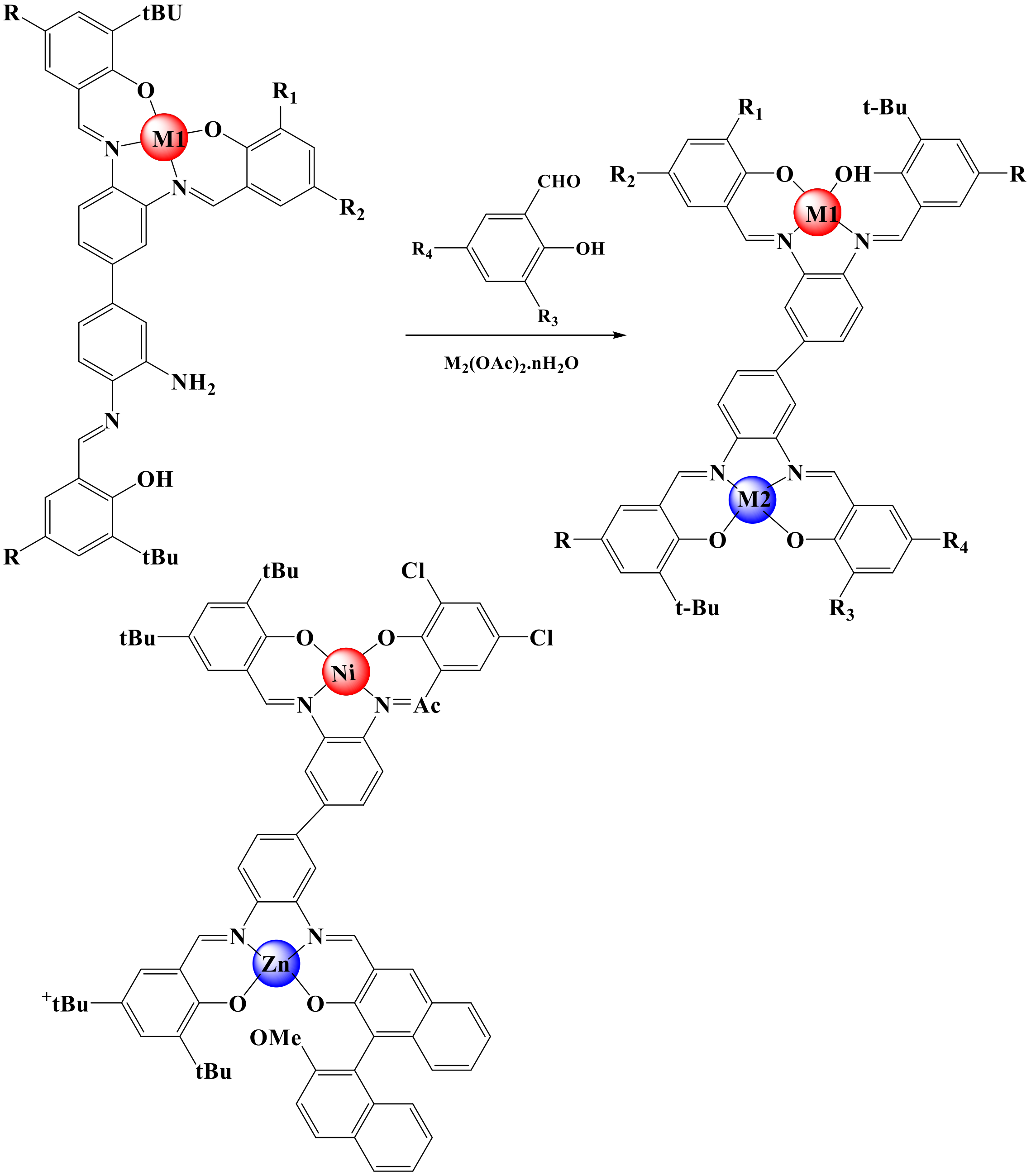
Scheme 2. Synthesis of Polymer 1(R_a= OC_8H_{17}, R_b= $OC_{16}H_{33}$).



Scheme 3. Synthesis of Polymer 2.



Scheme 4. Polymerisation of salophen (Poly-1) and Ni-salophen (Poly-1-Ni).

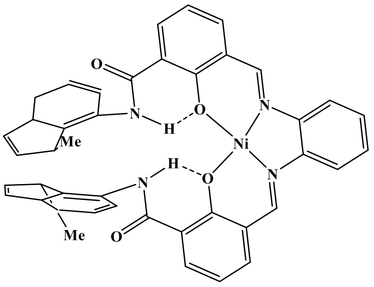


Scheme 5. Synthesis of heterobimetallic complexes.

CATALYTIC PROPERTIES

In recent years, the focus has expanded to the use of (metallo)salen building blocks for applications including (cooperative) multimetallic catalysis [26]. In order to create the multifunctional materials where both metal ions indicate different complementing functions like in the case of a determination and catalytic position, two various complexed ions could be useful. According to our information a direct and selective method for preparation of hetero-multimetallic salen structures was not priority and could have great potential in the domain of homogeneous catalysis and specially in cascade or tandem processes. Castillaet al. have presented a modular synthetic strategy for the formation of heterobimetallic salophen complexes that uses accessible monometallic triimine precursors synthetically [27] (Scheme 5).

A new field of metallofoldamers has been determined in which small end groups control the sense of helical folding, even in a case where the helical bias of the end group is a mismatched relation to the internal diamine. It will be necessary to utilise analogues in order to design foldamers so that they can be used in catalysis, and the metal center is not blocked by the ends of the helices. However, the large amount of the chiroptical properties indicates that the (P)-helix is the thermodynamically dominant conformation for a compound (Scheme 6) in solution [28].



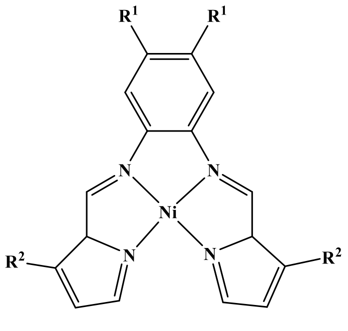
Scheme 6. A case of the helical bias of the end group.

Ren et al. introduced a well-defined homogeneous Ni(salophen) catalyst as a ‘‘metalloligand’’ in a porous MOF(metal–organic framework). The Ni(salophen) units and coordinatively unsaturated Cd active sites accessible through the open MOF channels were used to produce an efficient heterogeneous catalyst for the coupling reactions of CO_2 with epoxides under relatively mild situations. The MOF catalyst features a high local density of cooperative layer Ni(salophen) motifs, indicating improved catalytic application in relation to the monomeric homogeneous catalyst. This solid catalyst is recyclable easily and it is used again without any clear loss of catalytic activity even after being used three times. This work is a basis for a new strategy in the logical design of effective self-supported MOF catalysts for CO_2 absorption and insitu fixation based on functional metallosalens or metalloporphyrins [29].

NONLINEAR OPTICAL (NLO) PROPERTIES

Molecular-based second-order nonlinear optical (NLO) chromophores have been paid a lot of attention because of their potential applications inshowing optoelectronic technologies. Polling chromophores into high Tg polymer lattices has become the most probable approach toward molecular-based NLO instruments .The important prerequisitives to design suitable candidates are large $\mu \times \beta$ product and high thermal stability. In addition to organic NLO chro-mophores, the development of organometallic chromophores [30], that provides very large NLO responses [31] is hampered by moderate thermal stabilities. On the other hand, large hyperpolarizabilities have recently been investigated in long-range conjugated push pull metalporphyrin complexes [32]. The crystal structure, the synthesis, electronic and second-order nonlinear optical (NLO) properties of a new bis(salicylaldiminato) -nickel(II) Schiff-base complex are shown by Nakatani et al. The compound crystallizes in the space group $P\bar{1}$.They can determine the NLO properties by electric field induced second harmonic (EFISH) and by INDO/SCI-SOS calculation. This compound has been obtained by condensation of 4-(diethylamino)salicylaldehyde and 1,2-diamino-4,5-dinitrobenzene in the presence of nickel(II) chloride that shows the largest second-order NLO response reported for this family of bis(salicylaldiminato)nickel(II) metal complexes, with $\mu \times \beta$ value of 1530×10^{-48} cm^5 esu^{-1}. Also, a thermal stability up to 300 °C, represents potential uses of metal salen derivatives in poled polymers matrix with high Tg [33].

The synthesis, thermal stability, optical spectroscopic, electronic structure, and second-order nonlinear optical (NLO) properties of a new class of materials, based on planar $[N_4]Ni(II)$ complexes, are reported by Bella et al. The unsubstituted derivative shows the efficiency of urea in second-harmonic generation at 1.9 lm is 1.2 times. INDO/SCI-SOS quantum-chemical calculations can predict a sizeable molecular response and a considerable octupolar contribution to optical nonlinearity [34] (Scheme7).



Scheme 7. Synthesis of $[N_4]Ni(II)]$ complexes

5. Electrochemical propertises

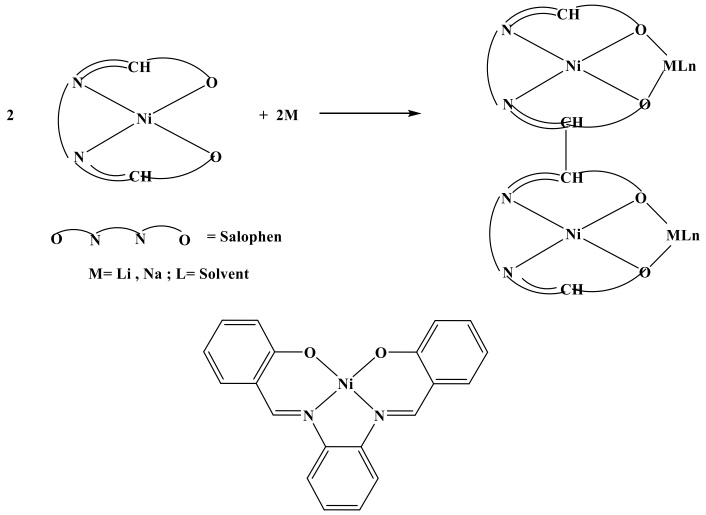
Transition metal complexes have an important participation in many electrochemical catalytic processes [35]. By cyclic voltammetry and controlled potential electrolysis, The electrochemical reduction mechanism of Ni(II)(salophen), Ni(L), in DMF has been investigated by Isse et al. The complex represents several redox processes. The first electron uptake, a ligand-based one-electron transfer at E°= - 1.39 V vs sce, will result in the formation of a nickel(II) radical anion, $[Ni(II)(L)]^-$, which dimerism quickly, giving rise to a product which consists of two Ni(L) units joined through a C-C bond. The dimer $[Ni(II)(L)]_2^{2-}$ undergoes anickel-centred reversible reduction process that happens at E° = -2.25 V vs sce to give $[Ni(I)(L)]_2^{4-}$. The dianion dimer can also be oxidized irreversibly at ca -0.8 V to restore the original Ni(L) complex. At the highest sweep rates dimerization is hampered so it allows thereversible reduction of the primary radical anion to $[Ni(I)(L)]^{2-}$ be observable [36].

The electrochemical reduction of the Schiff base ligands N,N′-1,2-ethylenebis- (salicylideneimine) and N,N′-1,2-phenylenebis(salicylideneimine) were studied in DMF by cyclic voltammetry, controlled potentia1 electrolysis And coulometry by Isse et al. The process includes a self-protonation mechanism thereby the two-electron reduction product, a cyclic derivative, are formed together with the conjugate base of the substrate, as a result of proton transfer from the substrate itself to the basic intermediates [37]. This study has shown that the peculiar electrochemical behaviour of Ni(salophen), that is considerably different from other nickel Schiff base complexes [38-39] and it can be interpreted so that the first electron uptake of Ni”L consists of the ligand instead of the metal center, so that a Ni(II) radical anion [N:’ L]-* is constructed. The latter dimerizes rapidly in orderto give a di-nickel(II) dimer in which two salophen units are joined by a carbon-carbon bond [40] (Scheme 8).

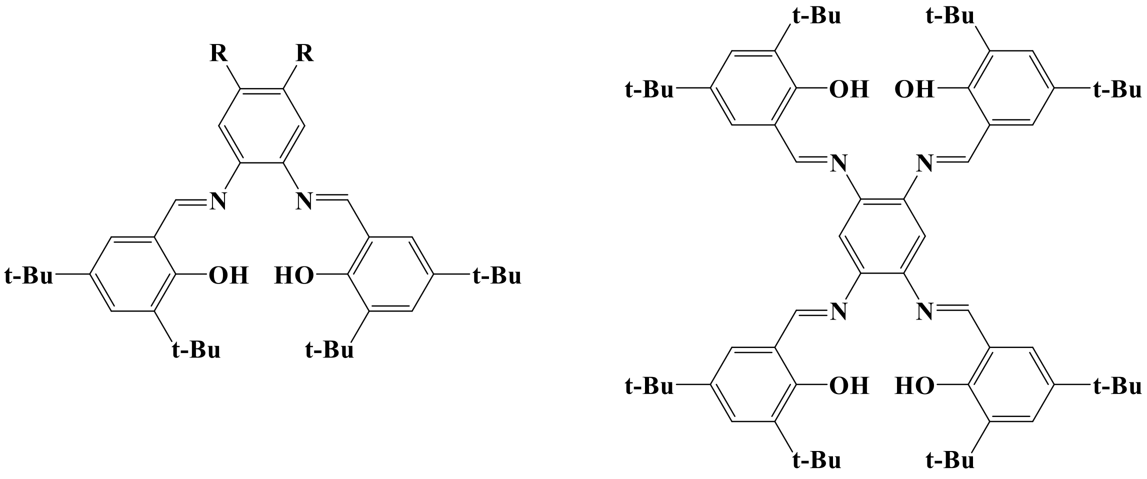
Rotthaus et al. have synthesized and determined crystal structure of The nickel(II) complexes of the mono and di-nuclearing Schiff base ligands H_2L^{OMe},H_2L^{NO2} and H_4L^{bis}. Cyclic voltammetry curves show that the electrochemical communication is considerably influenced by the substituent and the solvent. One of the one-electron oxidized species $[Ni(L^{OMe})]^+$ in CH_2Cl_2 is Phenoxyl radical with partial delocalization of the spin density on a metal orbital (contribution of 6.8%)while $[Ni(L^{NO2})]^+$ was found to disproportionate once it is generated. In the dinickel(II) complex of H_4L^{bis} , like $[Ni_2(L^{bis})]$, the phenylene spacer creates an electronic communication between the two metallic sites. Single oxidation of $[Ni_2(L^{bis})]$gives the delocalized phenoxyl radical $[Ni_2(L^{bis})]^+$, whose EPR signature is close to that of $[Ni(L^{OMe})]^+$. Double oxidation providesthe bis-{Ni^{II}-delocalized radical} species $[Ni_2(L^{bis})]^{2+}$. Each radical is located at a different metallic site but a weak and an important magnetic interaction will be between the paramagnetic centers. In the presence of pyridine, a complex including two ferromagnetically coupled nickel(III) ions will be obtained. The magnetic coupling has been calculated to 3.7 cm^{-1}, whereas the zero field splitting parameters are $|D| = 0.012\ cm^{-1}$and E = 0.They are in accordance with the large intermetallic distance (7.7 A ˚) and they are weak which are observed in the neutral precursor $[Ni_2(L^{bis})]$ [41] (Scheme 9).

Veggelet al. have been investigated the electrochemical properties of the complexed transition-metal cations in the heterodinuclear complexes and mono-transition-metal cation complexes by polarography and cyclic voltammetry. The half-wave potential relies on the nature of the transition-metal cation and the mode of coordination. The changes of the half-wave potential depends on the ring size and rigidity of the polyether cavity. The nickel complexe (Scheme 10) undergo a one-electron reduction [42].

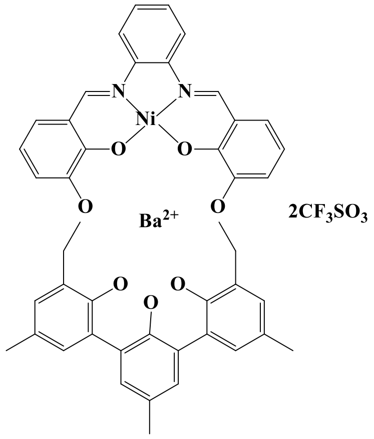
Schleyet al. prepared several monometallic salen complexes derived from O-functionalized diamines and used them as metalloligand in the synthesis of heterobimetallic complexes. Reactions of the conjugated nickel(II) salen complex 2a with metallocene derivatives provided soluble di- and trinuclear heterobimetallic complexes that depend on the use of stoichiometry Cyclovoltammetric experiments on 2a, 5a (Scheme 11) indicatedthe electron-withdrawing the effect of the $Tp^*{}_2La$ fragment. For all tested complexes, the catalytic activity in the epoxidation of the styrenewas low.



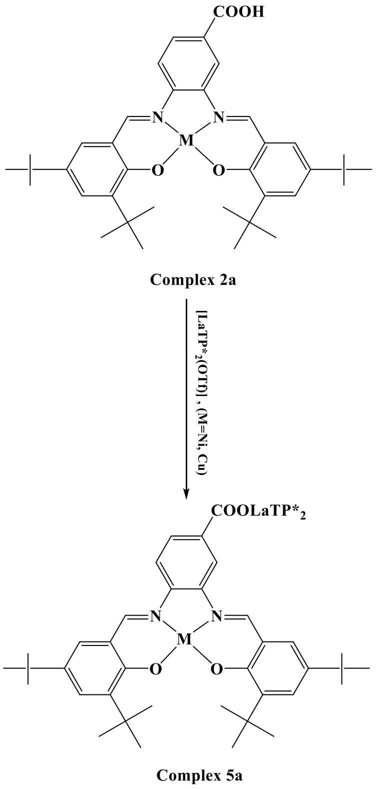
Scheme 8. Studied of the electrochemical reduction of Ni(salophen) with alkali metals.



Scheme 9. Mono and di-nuclearing Schiff base ligands.



Scheme 10. Heterodinuclear complexes and mono-transition-metal cation complexes.



Scheme 11. Synthesis of several monometallic salen complexes derived from O-functionalized diamines.

The cyclovoltammogram of the mononuclear nickel(II) complex 2a in dichloromethane represents two quasi -reversible signals at $E_{1/2}$ = 1.10 V and $E_{1/2}$ = 1.39 V (vs. SCE) that were determined as Ni^{II}/Ni^{III} and $Ni^{III}L/Ni^{III}L^{+}$.(L = salenligand). The analogous signals of the heterobimetallic complex 5a will be observed at $E_{1/2}$ = 1.09 V and $E_{1/2}$ =1.44 V (vs. SCE). The difference between equivalent redox potentials of the mono- and heterobimetallic complexes is rathersmall and only is significant in the case of $E_{1/2}(Ni^{III}L/Ni^{III}L^{+\cdot})$.The redox potential $E_{1/2}(Ni^{III}L/Ni^{III}L^{+\cdot})$ of the heterobimetallic complex 5a is 50 mV higher than the monometallic equivalent 2a, that shows a small electron-withdrawing influence caused by the early transition metal [43].

Mononuclear and heterodinuclear complexes of the salen-type ligand H_2LH_2 [H_2LH_2 = 2,2′-[1,2-dihydroxy- benzene-4,5-diylbis(nitrilomethylidine)]bis(3,5-di-tert-butylphenol)] were prepared by Schley et al. Also cyclic voltammetric investigations were done to determine the effect of the second transition metal complex fragment $[ZrCp*_2]^{2+}$on the metallo salen ligand. The cyclic voltammograms of [$NiLH_2$] and [$NiL(ZrCp_2)$] are described in Fig. 2. Moreover, the complexes were controlled in the catalytic epoxidation of styrene. The experiments revealed that the heterobimetallic complexes always display lower activity than the corresponding monometallic complexes, in accordance with further surveys in our group. when PhIO was used the decreased catalytic activity in the heterobimetallic complexes may be caused by more facile oxidation and decomposition. If the heterobimetallic complex is retained in solution, a steric effect of the bulky $[ZrCp*_2]^{2+}$ fragment may play a role in the catalytic process. Both the tert-butyl groups and the $ZrCp*_2$ fragment shield the catalytically active transition metal and can decrease the catalytic activity [44].

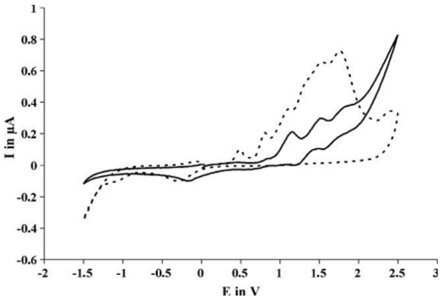
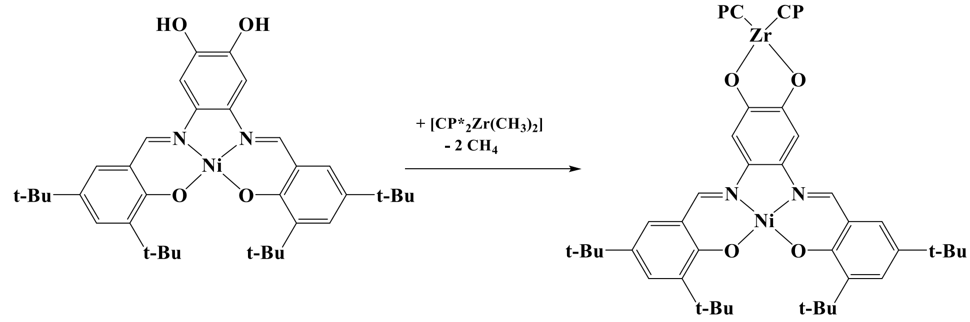


Fig. 2. Cyclic voltammograms of [$NiLH_2$] (_) and [$NiL(ZrCp_2)$] (**…**) in dichloromethane.

Zeolite-encapsulated complexes have interesting catalytic potential specially considering the activity for partial oxidation and stability. By a suitable choice of guest and host material, we can have further scope to design efficient catalyst systems. Salavati-Niasari et al understood that their geometry and the steric environment of the active sites will have an effect on catalytic properties of the complexes. HGNM (Host–Guest Nano composite Materialsare) stable enough to be reused and are suitable to be used as partial oxidation catalysts [45].



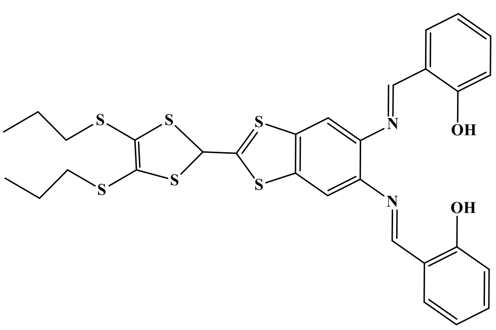
Scheme 12. Synthesis of Mononuclear and heterodinuclear complexes of the salen-type ligand H_2LH_2 [H_2LH_2 = 2,2′-[1,2-dihydroxy- benzene-4,5-diylbis(nitrilomethylidine)] bis(3,5-di-tert-butylphenol)].

MAGNETIC AND PHOTOPHYSICAL INVESTIGATIONS

Cosquer et al. have invented two simple synthetic steps permitted access to two TTF-based ligands, L^1 (Scheme 13), and L^2. The former led to six heterobimetallic dinuclear complexes of the formula [(L^1)MLn(hfac)$_3$] (where M=Cu^{II}, Ni^{II}; Ln=Y^{III}, Er^{III}, Yb^{III}). The UV−visible absorption properties have been investigated in a chloroform solution and rationalized by DFT and TD-DFT calculations. Upon oxidation, intramolecular SOMO → LUMO (20800 cm^{-1}) and SOMO−n → SOMO (11350 cm^{-1}) charge transfers have been observed, but the HOMO → LUMO charge transfers (20750 cm^{-1}) disappear. Through electrochemistry and absorption properties and the reducing agent, the reversibility of the oxidation has been confirmed. A ligand-centered fluorescence at 14450 cm^{-1} is Created by Irradiation at the HOMO → LUMO charge transfer energy of the dinuclear complex [(L^1)NiY(hfac)$_3$] [46].

BIOLOGICAL ACTIVITIES

We can observe the better antibacterial activity among Schiff base of pyrolidone, pyridone with O-phenylenediamine and their metal complexes [47]. Recently, the increase of microbial resistance to antibiotics which are used causes the more search for new compounds with potential effects against pathogenic bacteria. When heterocyclic compounds played an important role in regulating biological activities the most considerable advances will happen in medicinal chemistry. It is said that a lot of Schiff bases are important medicinally and we can use them to design medicinal compounds [48]. The derivatives of Schiff bases including nitro and halo have antimicrobial and antitumor activities [49]. Also the Antimicrobial and antifungal activities of different Schiff bases have been reported [50]. Fungi toxicity of some Schiff bases hase been investigated by Sahu et al.[51]. The high antimicrobial activities of some Schiff bases were reported by Gawad et al [52].



Scheme 13. Formula of the ligands L^1 Synthesis by Cosquer.

Akila et al. prepared the symmetrical mixed ligand Schiff bases by condensing o-phenylene-diamine with salicylaldehyde, o-phenylenediamine with benzaldehyde and their use to prepare mononuclear Schiff base mixed ligand complexes have been shown in this article. The results of the biological screening of the ligands and their metal complexes demonstrated that the antibacterial activities of the chelated ligands increase as compared to the free ligands [53].

Raman et al. synthesized and characterized of Schiff base ligand(L) derived from β-ketoanilide and furfural with o-phenylenediamine and diethylmalonate. The in vitro antimicrobial activity of the complexes of the ligand and its ligand was investigated by disc diffusion method.The results that were obtained from antifungal and antibacterial tests indicated that all the complexes are more active towards fungi than bacteria. It became clear that complexes have higher antimicrobial activity than that of free ligand [54].

A tetraaza macrocyclic Schiff base (L), synthesized from 1,2-(diimino-4′ -antipyrinyl) -1,2-diphenylethane and *o*-phenylenediamine by Raman et al. acts as a tetradentate ligand and forms solid cationic complexes with Ni(II) salts in ethanol. All the synthesized compounds were describedthrough microanalytical data, magnetic susceptibility measurements, IR, UV-Vis., ^{1}H NMR, ^{13}C NMR, ESR and mass spectral techniques. The investigated compounds and uncomplexed metal salts were experimented against bacteria like Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa and Shigella flexneri. The activity of the metal salts is higher than the metal chelates and the free ligand [55].

The antibacterial activities of the Schiff base derived from N,N'-1,2-phenylene-bis(2-hydroxy-1-naphthaldimine)were investigated by Prakash et al.biologically, these complexes are active against bacteria fungus viz. E. coli and S. aureus C.albicans so these may be considered as suitable antibacterial agents and fungicides [56].

Halli et al. synthesized and characterized complexes Ni(II) derived from E-N′-(3,4,5-trimethoxybenzylidene)benzofuran-2 carbohydrazide and ortho-phenylenediamine/ 2,6 diamino-pyridine, The antifungal and antibacterial activities of the complexes and ligands have been screened against bacteria Escherichia coli and Staphylococcus aureus and against fungi Aspergillus niger and Aspergillus flavus [57].

Sherifand Abdel-Kader have synthesized Schiff bases derived from condensation of 1,4-phenylenediamine and benzopyrone derivatives. By using Escherichia coli and Staphylococcus capitis the antibacterial activity was screened but by using Aspergillus flavus and Candida albicans, the antifungal activity was investigated. The results showed that the tested complexes have antibacterial properties [58].

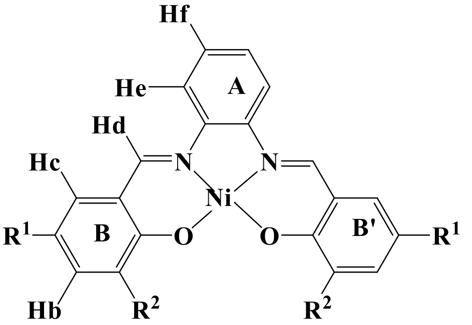
The complexes of the Schiff base including Ni(II), Co(II), Cu(II) and Zn(II)were derived from vanillinidene-4-aminoantipyrine and *o*-phenylenediamine were synthesized and characterized by Sivasankaran Nair and Arish. The in vitro biological screening effects of the synthesized compounds were tested against the bacterial species, Escherichia coli, Bacillus subtilis, Pseudomonas aeruginosaand Staphylococcus aureus; fungal species, Aspergillus niger, Aspergillus Candida albicansandflavus by using the disc diffusion method and the results show that the metal complexes are more biological active than the ligand [59].

MISCELLANEOUS PROPERTIES

Joshaghani et al. have investigated the complexation reaction between Cu^{2+},Co^{2+} and Ni^{2+} metal cations with N,N′-bis(salicylidene)-1,2-phenylenediamine (salophen), in three nonaqueous polar solvents such as: dimethyl sulfoxide (DMSO), acetonitrile (AN), methanol (MeOH) and two binary mixtures of AN:MeOH and AN:DMSO at 25 °C by conductometric and spectrophoto-metric methods. By considering the temperature dependence on stability constants and the results for all metal ion complexes, the values of the thermodynamic parameters (ΔH°, ΔS° and ΔG°) for complexation reactions were obtained. So the value of ΔH°, ΔS° and ΔG° are solvent dependent [60].

Tamaki et al. have reported that the change in the surface alignment of [Ni(salophen)] substituted by different number of alkyl groups on HOPG. The increase in the number of substituted long alkyl groups caused the increase of the solubility of the complex toward organic solvent, but the tendency of the decrease is to aggregate. This influence is considered as a reason to explain why 2 with four alkyl groups covered HOPG surface with monomers, while 1 with two alkyl groups covered with dimers [61] (Scheme 14).

A series of metal complexes with salophen and salen derivatives as ligands Schiff bases has been prepared and fully characterized, including three X-raycrystal structures by Arola-Arnal et al. The interactions of these complexes with duplex and human telomeric quadruplex DNA have been investigated by fluorescence resonance energy transfer(FRET), fluorescent intercalator displacementtests, and in one case of circular dichroism. These researches have shown the square-planar metal complexes to be the most suitable quadruplex DNA stabilizers, speciallythe planar nickel(II) salophen complexes 3 and 4 are the best quadruplex DNA binders and telomerase inhibitors. Also the FRET competition investigations have shown the complexes to have a high degree of selectivity for the DNA quadruplex versus duplex DNA. These findings have permitted us to establish the most important properties that metal complexes should have to interact with quadruplex DNA selectively. This will have the value of determining the best strategy to prepare metal complexes as potential anticancer drugs [62].



R^1 = octyl, R^2= Ha ; [Ni(2C_8-salophen)] (1)

R^1 = R^2 = octyl ; [Ni(4C_8-salophen)] (2)

Scheme 14. Structure of [Ni(salophen)] substituted by different number of alkyl groupson HOPG.

l-Ascorbic acid (Vitamin C) is an antioxidant, preventing color changes and alterations of aroma and flavor as well as expanding the storage time of the products [63]. This vitamin is among the compound of major biological significance, it has a key role in the protection against biological oxidation processes, the treatment and prevention of common cold, mental diseases and infertility, the treatment and prevention of Scurvy, but it is also important in the regulation of the immunological system and in tissue reconstruction, which is useful for the formation of collagen. Potentiometric membrane sensors for periodate based on amodern synthesized and well characterized Ni(II)-Schiff bases with high sensitivity and good selectivity were developed and was used in batch and hydrodynamic modes of operation. The sensors have the advantages of rapid response, logical selectivity, low cost and possible interfacings with computerized and automated systems. Interfacing the sensor in a flow injection analysis system gives sufficient speed of analysis, good reproducibility, high sample throughout and excellent response characteristics. Direct analysis of ascorbic acid was possible under static and hydrodynamic condition of operations with a linear range 2.0–13gmL−1 with a sample rate ∼50–55 sample h−1 [64]. Some of the analytical properties of improved method were compared with other techniques based on different methods, this process is simple and inexpensive because Most of these methods, use the expensive instruments, [65–69], there is no selectivity [69-71], involving careful control of the reaction situations or derivatization reactions [69-70,72-73], and they need time-consuming pretreatment steps that are not easily applied to turbid or colored samples and affect their usefulness for routine analysis [69-70].

Acknowledgments **:***Payame Noor University, for providing necessary facilities to carry out the work is gratefully acknowledged.*

REFERENCES

1. H. Kargar, R. Kia, M. N. Tahir, A. Sahraei, *Acta Crystallogr., Sect. E.*, **66**, 1246 (2010).
2. A. Adabiardakani, M. Hakimi, H. Kargar, *World Appl. Programming*, **2**, 472 (2012).
3. A. Sahraei, H. Kargar, R. Kia, I. U. Khan, *Acta Crystallogr., Sect. E.*, **67,** o636 (2011).
4. A. Sahraei, H. Kargar, R. Kia, M. N. Tahir, *Acta Crystallogr., Sect. E.*, **67,** m82 (2011).
5. R. A. Sheldon, W. C. E. Arends, A. Dijksman, *Catal. Today*, **57**, 157 (2000).
6. R. A. Sheldon, R. S. Downing, *Appl. Catal. A: Gen.*, 189 (1999).
7. J. C. Medina, N. Gabriunas, A. Paez-Mozo, *J. Mol. Catal. A. Chem.*, **115**, 233 (1997).
8. M. Palucki, P. J. Pospisil, W. Zhang, E. N. Jacobsen, *J. Am. Chem. Soc.*, **116**, 9333 (1994).
9. S. M. Kim, J. S. Kim, B. C. Sohn, Y. K. Kim, Y. Y. Ha, *Mol. Cryst. Liq. Cryst.*, 371 (2001).
10. K. Bergstad, H. Grennberg, J. E. Backvall, *Acta Chem. Scand.*, **59,** 741 (1999).
11. M. B. Gholivand, F. Ahmadi, E. Rafiee, *Electroanalysis*, **18**, 1620 (2006).
12. M. K. Amini, J. H. Khorasani, S. S. Khaloo, S. Tangestaninejad, *Anal. Biochem*., **320**, 32 (2003).
13. M. R. Al-Saraj, S. M. Saadeh, M. S. Abdel-Latif, *Anal. Lett.*, **36**, 2417 (2003).
14. M. B. Gholivand, F. Ahmadi, E. Rafiee, *Separ. Sci. Technol.*, **41**, 315 (2006).
15. M. B. Gholivand, P. Niroomandi, A. Yari, M. Joshaghani, *Anal. Chim. Acta*, **538**, 225 (2005).
16. M. B. Gholivand, F. Ahmadi, E. Rafiee, *Separ. Sci. Technol.*, **42**, 897 (2007).
17. S. Kashanian, M. B. Gholivand, F. Ahmadi, A. Taravati, A. Hosseinzadeh-Colagar, *Spectrochim. Acta Part A.*, **67**, 472 (2007).
18. K. H. Reddy, P. S. Reddy, P. R. Babu, *Transition Met. Chem.*, **25**, 154 (2004).
19. I. Manners, *Science*, **294**, 1664 (2001).
20. V. Chandrasekhar, A. Athimoolam, *Org. Lett.*, **4**, 2113 (2002).
21. D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.*, **100**, 2537 (2000).
22. M. J. MacLachlan, M. Ginzburg, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, G. A. Ozin, I. Manners *Sci.*, **287**, 1460 (2000).
23. O. Lavastre, I. Illitchev, G. Jegou, P. H. Dixneuf, *J. Am. Chem. Soc.*, **124**, 5278 (2002).
24. A. C. W. Leung, J. H. Chong, B. O. Patrick, M. MacLachlan, *Macromolecules*, **36**, 5051 (2003).
25. H. Fukumoto, K. Yamane, Y. Kase, T. Yamamoto, *Macromolecules*, **43**, 10366 (2010).
26. G. M. Sammis, H. Danjo, E. N. Jacobsen, *J. Am. Chem. Soc.*, **126**, 9928 (2004).
27. A. M. Castilla, S. Curreli, E. C. Escudero-Adan, M. Martınez Belmonte, J. Benet-Buchholz , W. A. Kleij, *Org. Lett.*, **11**, 22 (2009).
28. Z. Dong, J. N. Plampin, G. P. A. Yap, J. M. Fox, *Org. Lett.*, **12**, 18 (2010).
29. Y. Ren, Y. Shi, J. Chen, S. Yang, C. Qi, H. Jiang, *RSC Adv.*, **3**, 2167 (2013).
30. N. J. Long, *Angew, Chem,. Int. Ed.*, **34**, 21 (1995).
31. I. R. Whittall, M. G. Humphrey, A. Persoons, S. Houbrechts, *Organometallics*, **15**, 1935 (1996).

32. S. M. Lecours, H-W. Guan, S. G. Dimagno, C. H. Wang, M. J. J. Therien, *J. Am. Chem. Soc.*, **118**, 1497 (1996).
33. K. Nakatani, I. Maltey-Fanton, A. Delaire, *J. Chem. Mater.*, **11**, 995 (1999).
34. S. D. Bella, I. Fragal, A. Guerri, P. Dapporto, K. Nakatani, *Inorg. Chim. Acta*, **357**, 1161 (2004).
35. O. N. Efimov ,V. V. Strelets, *Coord. Chem. Rev*., **99**, 15 (1990).
36. A. A. Isse, A. Gennaro, E. Vianello, *Electrochim. Acta.* , **37**, 113 (1992).
37. A. A. Isse, A. Cennaro, E. Vianello, *Electrochim. Acta.*, **42**, 2065 (1997).
38. C. Gosden, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroad. Chem*., **117**, 101 (1981).
39. P. Zanello, A. Cinauantini, *Transition Met. Chem.*, **10**, 370 (1985).
40. A. A Isse, A. Gennaro, E. Vianello, *Electrochim. Acta*., **37**, 113 (1992).
41. O. Rotthaus, O. Jarjayes, C. Philouze, C. P. Del Valleband, F. Thomas, *Dalton Trans.*, 1792 (2009).
42. F. C. J. M. v. Veggel, S. Harkema, M. Bas, W. Verboom, C. J. van Staveren, G. J. Gerritsma, D. N. Reinhoudt, *Inorg. Chem*., **28**, 1133 (1989).
43. M. Schley, S. Fritzsche, L. P. onnecke, E. Hey-Hawkins, *Dalton Trans.*, **39**, 4090 (2010).
44. M. Schley, P. Lönnecke, E. Hey-Hawkins, *J. Organomet. Chem.*, **694**, 2480 (2009).
45. M. Salavati-Niasari, M. Shakouri-Arani, F. Davar, *Microporous Mesoporous Mater.*, **116**, 77 (2008).
46. G. Cosquer, F. Pointillart, B. L. Guennic, Y. L. Gal, S. Golhen, O. Cador, L. Ouahab, *Inorg. Chem.*, **51**, 8488 (2012).
47. S. Gaur, *Asian J. Chem*., **15,** 250 (2003).
48. S. K. Chakraborti, De. B. Kumar, *J. Indian Chem. Soc*., 137 (1973).
49. T. D. Chaudhari, S. S. Subnis, *Bull. Haskins Inst.*, **4**, 85 (1986).
50. S. Shah, R. Vyas, R. H. Mehta, *J. Indian Chem. Soc*., **69**, 590 (1992).
51. K. Sahu, R. K. Behera, R. C. Pathaik, A. Nayak, G. B. Behera, *Indian J. Chem*., **18B**, 557 (1979).
52. M Abdul-Gawad, Y. M. Issa, S. M. Abd-Alhamid, *Egypt J. Pharm. Sci.* 34 (1993) 219.
53. E. Akila, M. Usharani, S. Vimala, R. Rajavel, *Chem. Sci. Rev. Lett.*, **1**, 181 (2012).
54. R. Natarajan, J. A. Ramaraj, J. Jeyasekaran, *J. Iran Chem. Res.*, **3**, 83 (2010).
55. N. Raman, A. Kulandaisamy, K. Jeyasubramanian, *Synth. React. Inorg. Met-Org. Chem.*, **34**, 17 (2004).
56. D. Prakash, C. Kumar, K. R. R. P. Singh, *Indian Chem. Soc.*, **85**, 371 (2008).
57. M. B. Halli, V. B. Patil, M. Kinni , R. B. Sumathi, *J. Coord. Chem.*, **64**, 651 (2011).
58. O. E. Sherif, N. S. Abdel-Kader, *Spectrochim. Acta Part A*, 519 (2014).
59. M. S. Nair, D. Arish, *Trans. Indian Inst. Met.*, **64**, 287 (2011).
60. M. Joshaghani, M. B. Gholivand, F. Ahmadi, *Spectrochim. Acta Part A*, **70**, 1073 (2008).
61. Y. Tamaki, K. Tomono, Y. Hata, N. Saita, T. Yamamoto, K. Miyamura, *Bull. Chem. Soc. Jpn.*, **85**, 592 (2012).
62. A. Arola-Arnal, J. Benet-Buchholz, S. Neidle, R. Vilar, *Inorg. Chem.*, **47**, 11910 (2008).
63. M. W. Davey, M. Van Montagu, D. Inze, M. Sanmartin, A. Kanellis, N. Smirnoff, I. J. J. Benzie, J. J. Strain, D. Favell, J. Fletcher, *Sci. J. Food Agric*., **80**, 825 (2000).
64. A. A. Aziz, A. H. Kamel, *Talanta*, **80**, 1356 (2010).
65. A. Rodríguez-Bernaldo de Quirós, M. Fernández-Arias, J. López-Hernández, *Food Chem.*, **116,** 509 (2009).
66. A. Balaguer, A. Chisvert, A. Salvador, *J. Sep. Sci.*, **31,** 229 (2008).
67. Y. Peng, Y. Zhang, J. Ye, *J. Agric. Food Chem.*, **56**, 1838 (2008).
68. T. Wu, Y. Guan, J. Ye, *Food Chem.*, **100**, 1573 (2007).
69. T. R. L. C. Paixao, M. Bertotti, *J. Pharm. Biomed. Anal.*, **46**, 528 (2008).
70. D. G. Themelis, P. D. Tzanavaras, F. S. Kika, *Talanta*, **55**, 127 (2001).
71. A. Abbaspour, A. Khajehzadeh, A. Noori, *Anal. Sci.*, **24**, 721 (2008).
72. Y. Peng, Y. Zhang, J. Ye, *J. Agric. Food Chem.*, **56,** 1838 (2008).
73. T. Wu, Y. Guan, J. Ye, *Food Chem.*, **100**, 1573 (2007).