

extent of experimental uncertainties. Figure 7 shows typical dependencies, on the angle of incidence, of normalized RSC's of the same system as for the Figure 6. According to Figure 7, n_2 is least sensitive to Δ and most sensitive to Ψ for wide range of ϕ_1 . At $\phi_1=55^\circ$, k_2 and τ_2 are most sensitive to R and Ψ , respectively, while τ_2 is least sensitive to Δ . Thus, for example, the experimental error in Δ would not affect the values of n_2 and τ_2 as much as the errors in Ψ and R . This agrees with the observations made earlier based on the shapes of the constant Ψ , Δ , and R surfaces. If the thickness of the film, τ_2 , is the most important property to be determined, then Ψ and R should be carefully measured.

From these RSC's, it can be clearly seen that the properties of the film are very sensitive to Ψ and R at $\phi_1 \approx 70^\circ$. At this angle of incidence, any experimental errors in Ψ , and R would be magnified in n_2 , k_2 , and τ_2 , thus making experiment extremely difficult. Moreover, it is also noted that the measurement of R is most susceptible to fluctuations in the experimental set-up. This agrees with the previous conclusion of Paik *et al.*⁴ in which $\phi_1 \approx 55^\circ$ is preferred over $\phi_1 \approx 70^\circ$ used in the conventional two-parameter ellipsometry.

The sensitivity coefficients are also affected by the refractive index of the ambient medium, n_1 . As n_1 increases, the RSC's generally increase slightly in magnitudes although the overall dependencies on ϕ_1 are similar to Figure 7. The optical properties of the substrate also show minor effect on the RSC's.

In order to determine the optimum experimental conditions, the measurements should be sensitive enough to discern the films of different physical properties. At the same time, the film properties to be determined should not be too sensitive to the experimental errors in the measurements. Therefore, both of the FSC's and RSC's should be carefully examined to find the optimum compromise.

In this paper, we clarified the nature of the solutions for the film properties obtained by the TPE by closely examining the constant Ψ , Δ , and R surfaces. We also identified,

through the FSA, the properties of the film which affect most the ellipsometric-reflectometric measurements. Furthermore, it is shown that the RSA can provide a measure of estimating errors in film properties arising from the experimental uncertainties in measurements. It is also shown that the optimum experimental conditions can be determined by sensitivity analysis.

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Synthesis of New Tetraaza Macrocyclic Ligands with Cyclohexane Rings and their Ni(II) and Cu(II) Complexes

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The tetraaza macrocyclic ligand 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosa-2,12-diene(B), that contains two cyclohexane rings, has been prepared as its dihydroperchlorate salt by the nontemplate condensation of methyl vinyl ketone with 1,2-diaminocyclohexane and perchloric acid. Reduction of B with sodium borohydride produces 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosane(C). Square planar Ni(II) and Cu(II) complexes of B and C have been prepared by the reaction of the metal ions and the ligands. Synthesis, characterization, and the properties of the ligands and their metal complexes are reported.

Introduction

Synthetic polyaza macrocycles and their metal complexes

often exhibit unusual chemical properties which enable practical applications of these compounds.¹⁻¹³ Since the properties of the macrocyclic compounds are correlated with struc-

tural characteristics of the ligands, many efforts have been made to obtain new types of macrocyclic compounds, which are expected to exhibit specific properties.¹¹⁻¹⁷ Structural parameters which can be varied include the metal ion, ring size, degree of unsaturation, and types and number of substituents on the macrocyclic rings.

Although a majority of unsaturated macrocyclic ligands have been prepared by metal ion template condensation of ketones and multiamines, some of them have also been obtained by nontemplate reactions of α , β -unsaturated ketones with amines.¹⁸⁻²³ For example, the 14-membered macrocycle A has been prepared by the reaction of methyl vinyl ketone with ethylenediamine.^{18,19} However, most macrocycles obtained by the nontemplate procedures have only methyl groups or have no substituents at the carbon atoms of N-C-C-N linkages. Therefore, we have been interested in the synthesis of the new macrocyclic ligand 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16,4,0^{1,18},0^{7,12}]docosa-2,12-diene(B), that contains two cyclohexane rings at the macrocyclic backbone, by the nontemplate reaction of methyl vinyl ketone with 1,2-diaminocyclohexane. The saturated ligand 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16,4,0^{1,18},0^{7,12}]docosane(C) has also been prepared by reduction of B·2HClO₄ with NaBH₄. This paper reports the synthesis and properties of the ligands and their Ni(II) and Cu(II) complexes.

Experimental

Materials and Measurements

All chemicals used in synthesis were of reagent grade. Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer using Nujol mulls and KBr disks. Conductivities were calculated from electrical resistance measurements using a Metrohm Herisau Conductometer E518. Electronic spectra were obtained using a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. NMR spectra were obtained with a Bruker WP 300 FT NMR spectrometer. Mass spectra were recorded on a Kratos 25-RFA GC-Mass spectrometer. Ele-

working and counter electrodes were platinum, and the reference electrode was SCE. All measurements were made on 0.1 M (n-Bu)₄ NClO₄ acetonitrile solutions.

Synthesis

B·2HClO₄·H₂O. To a cooled(0-4°C) ethanol (200 ml) solution of 1,2-diaminocyclohexane (35 ml) was added dropwise 60% perchloric acid (25 ml) with stirring. Methyl vinyl ketone (22 ml) was added over a period of 1 h to the solutions at 0-4°C, and then white precipitates of the product were formed. The resulting suspension was allowed to warm up to ambient temperature and then stored overnight to complete crystallization. The white product was filtered off, washed with ethanol, and dried under vacuum. Yield: ~25%. m.p.: 203° (decomposed). Anal. Calcd for C₂₀H₄₀N₄Cl₂O₉: C, 43.6; H, 7.31; N, 10.2%. Found: C, 43.9; H, 7.00; N, 10.0%.

C. To a cooled (0-4°C) methanol (50 ml) suspension of B·2HClO₄ (10.7 g) were slowly added NaOH (1.60 g) and NaBH₄ (1.81 g) over a period of 2 h. The resulting mixture was stirred for 2 h at room temperature and then heated at reflux for 20 min. After cooled, the solution was filtered and NaOH (4.8 g) in water (100 ml) was added to the filtrate. The solution was stirred until precipitation of the product was complete. The white product was filtered, washed with water, and air-dried. The product was recrystallized from hot methanol-water (4 : 1) mixture. Yield: ~90%. m.p.: 221°C. Anal. Calcd for C₂₀H₄₀N₄: C, 71.4; H, 12.0; N, 16.7%. Found: C, 71.5; H, 12.2; N, 16.4%.

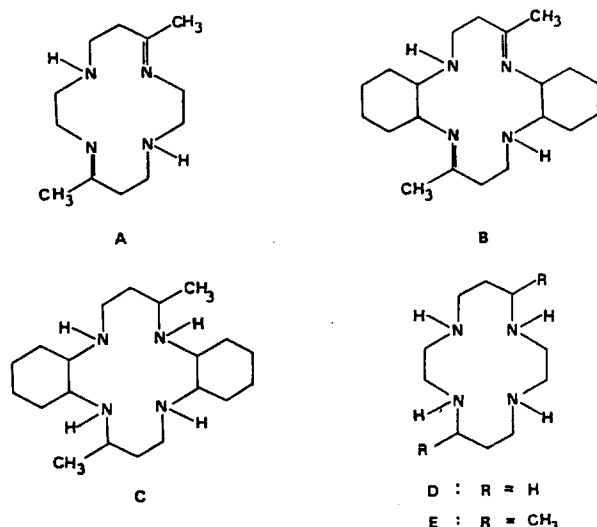
[Ni(B)](ClO₄)₂·H₂O. A methanol suspension of Ni(OAc)₂·4H₂O (3.5 g) and B·2HClO₄·H₂O (7.5 g) was heated at reflux for 30 min, and then yellow solids were precipitated. After it was cooled to room temperature, the yellow product was filtered, washed with methanol, recrystallized from hot acetonitrile-water (3 : 2) mixture, and air-dried. Yield: >90%. Anal. Calcd for NiC₂₀H₃₈N₄Cl₂O₉: C, 39.5; H, 6.25; N, 9.21%. Found: C, 39.2; H, 5.87; N, 8.96%.

[Ni(C)](ClO₄)₂. A methanol (50 ml) solution of Ni(OAc)₂·4H₂O (3.5 g) and C (4.7 g) was heated at reflux for 30 min and then cooled to room temperature. Excess amount of NaClO₄ was added to the solution and yellow crystals formed. The yellow product was filtered, washed with methanol, recrystallized from hot acetonitrile-water (3 : 2) mixture, and air-dried. Yield: >90%. Anal. Calcd for NiC₂₀H₄₀Cl₂O₈: C, 40.43; H, 6.11; N, 9.43%. Found: C, 40.0; H, 6.11; N, 9.24%.

[Ni(L)](PF₆)₂ (L=B or C). Excess amount of NH₄ PF₆ was added to a warm acetonitrile (15 ml) suspension of [Ni(L)](ClO₄)₂ (0.5 g), and then the complex was dissolved and white NH₄ ClO₄ was precipitated. After the solids were removed by filtration, water (25 ml) was added to the filtrate. The resulting solution was kept in a refrigerator until the yellow crystals formed. The product was filtered, washed with methanol, and air-dried.

[Cu(B)](ClO₄)₂. This red complex was prepared by a procedure similar to that for [Ni(B)](ClO₄)₂·H₂O using Cu(OAc)₂·H₂O (2.8 g) in place of Ni(OAc)₂·4H₂O. Yield: >90%. Anal. Calcd for CuC₂₀H₃₆N₄Cl₂O₈: C, 40.4; H, 6.10; N, 9.42%. Found: C, 40.0; H, 6.11; N, 9.24%.

[Cu(C)](ClO₄)₂·H₂O. This red compound was prepared by a method similar to that for [Ni(C)](ClO₄)₂ using Cu(OAc)₂·H₂O (2.8 g) instead of Ni(OAc)₂·4H₂O. Yield: >90%. Anal. Calcd for CuC₂₀H₄₂N₄Cl₂O₉: C, 38.9; H, 6.86; N, 9.08%.

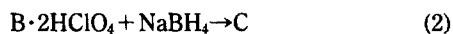
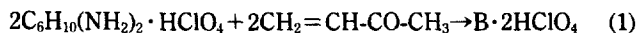


mental analyses were performed by Kolon R & D Center. Cyclic voltammetric measurements were performed using a Yanaco Voltammetric Analyzer P-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder. The

Found: C, 39.4; 6.73; N, 8.99%.

Results and Discussion

Ligands. The reaction (Eq. 1) of equimolar mixtures of 1,2-diaminocyclohexane ($C_6H_{10}(NH_2)_2$), perchloric acid, and methyl vinyl ketone in absolute ethanol solution is expected to produce a mixture of the two unsaturated macrocycles B having *trans* imino groups and its *cis* isomer. We isolated only $B \cdot 2HClO_4$ as a major product in this reaction, but the salt having *cis* imino groups could not be obtained. It has also been reported that the reaction of methyl vinyl ketone with ethylenediamine appears to be stereospecific giving the macrocycle A with *trans* imino groups.¹⁸ All attempts to obtain the macrocycle B by metal ion template condensation reaction in the absence of the acid were unsuccessful. When Ni(II) ion, instead of perchloric acid, was added to an ethanolic solution containing 1,2-diaminocyclohexane and methyl vinyl ketone, we observed no evidence indicating that a macrocyclic complex had formed. This indicates that hydrogen ion plays an important role in the formation of the macrocycle. However, no attempt is made in this work to elucidate the mechanism for the reaction. Reduction (Eq. 2) of $B \cdot 2HClO_4$ by $NaBH_4$ in methanol solution gives the saturated macrocycle C.



The compounds $B \cdot 2HClO_4$ and C are white solids and very stable at room temperature. The salt $B \cdot 2HClO_4$ is soluble in DMSO but is unstable and soon decomposed in the solution. The ligand C is readily soluble in chloroform and alcohols. Infrared spectrum of $B \cdot 2HClO_4$ shows $\nu_{C=N}$ and ν_{N-H} bands at 1662 and 3170 cm^{-1} , respectively. The spectrum of C shows a ν_{N-H} band at 3260 cm^{-1} but do not show any band around 1660 cm^{-1} assignable to $\nu_{C=N}$. The mass spectrum of C gives m/e value 336, which is in accord with the molecular weight of the ligand. The ligand C contains ten chiral centers so that numbers of diastereoisomeric structures are theoretically possible. However, 1H -NMR spectrum of C showed only one doublet centered at δ 0.96 ppm for the two methyl groups. This strongly indicates that the ligand prepared in this work is one of the diastereoisomers with two equatorially oriented methyl groups.^{18,19} The peaks of the ring protons are very complicated and difficult to interpret. ^{13}C -NMR spectrum (Figure 1) of D shows ten resonances indicating that the ligand contain ten pairs of nonequivalent carbon atoms. This observation is in support of the symmetric arrangements of the carbon atoms in the ligand. The carbon peaks of cyclohexane rings are observed at 24.7, 25.4, 30.3, 30.9, 57.3, and 63.2 ppm. The peak of methyl groups is observed at 16.7 ppm. Peaks at 36.2, 42.8, and 46.7 ppm are due to the carbons of the N-C-C-C-N linkages. NMR spectra of $B \cdot 2HClO_4$ were not obtainable because of its instability in solutions.

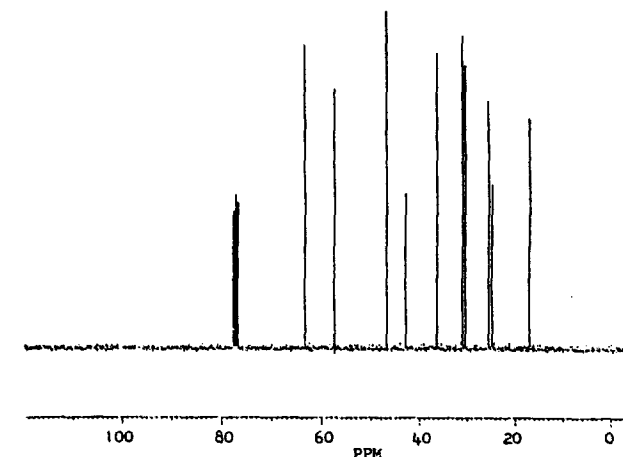


Figure 1. ^{13}C -NMR spectrum of C in $CDCl_3$ solution.

Complexes. The complexes $[M(L)](ClO_4)_2$ ($M=Ni(II)$ or $Cu(II)$; $L=B$ or C) were readily prepared by reaction of the metal ions with the ligands, followed by addition of excess sodium perchlorate, in methanol solutions. The Ni(II) and Cu(II) complexes are soluble in nitromethane, acetonitrile, and DMF.

Table 1. Spectral and Molar Conductance Data of the Macrocyclic Ligands and their Ni(II) and Cu(II) Complexes

Compound	IR spectra, cm^{-1}		Electronic spectra ^a			Molar conductance	
	ν_{N-H}	$\nu_{C=N}$	λ_{max} , nm(ϵ , $M^{-1}cm^{-1}$)			Λ_M , $\Omega^{-1}mol^{-1}cm^2$	
$B \cdot 2HClO_4$	3170	1662					
C	3260						
$[Ni(A)]^{2+e}$			448(87)	448(82) ^b			
$[Ni(B)](ClO_4)_2$	3202	1643	439(77)	440(73) ^b	442(73) ^c	212 ^b	295 ^c
$[Ni(C)](ClO_4)_2$	3185		463(73)	459(70) ^b	465(66) ^c	205 ^b	256 ^c
$[Ni(E)]^{2+f}$			467(64)	460(22) ^b			
$[Cu(A)]^{2+e}$			508(87) ^b				
$[Cu(B)](ClO_4)_2$	3260	1655	503(146)	534(141) ^b		201 ^b	
			527(148) ^c	545(140) ^d			
$[Cu(C)](ClO_4)_2$	3208		487(113)	508 ^b		200 ^b	
			508(150) ^c	519(419) ^d			
$[Cu(E)]^{2+f}$			508(92) ^b				

^a In nitromethane solutions at 25°C otherwise unspecified. ^b In aqueous solutions. ^c In acetonitrile solutions. ^d In DMF solutions.

^e Ref. 18. ^f Ref. 24.

trile, and water. The complexes are extremely stable in crystalline solid states and quite stable even in highly acidic solutions. Electronic spectra of the Ni(II) and Cu(II) complexes in 0.3 M HNO₃ solutions showed that only 1-2% of the complexes were decomposed in 10 h at 20°C.

The infrared spectra (Table 1) of the complexes are similar to those of the free ligands. Molar conductances in acetonitrile and aqueous solutions show the Ni(II) and Cu(II) complexes to be 1:2 electrolytes. The electronic spectra of [Ni(B)]²⁺ and [Ni(C)]²⁺ in solutions exhibit a single *d-d* transition band at 439-442 nm ($\epsilon = 73\text{--}77 \text{ M}^{-1}\text{cm}^{-1}$) and 459-463 nm ($\epsilon = 66\text{--}73 \text{ M}^{-1}\text{cm}^{-1}$), respectively. The spectra are quite similar to those for the square planar Ni(II) complexes with A¹⁸ and E²⁴, indicating that ligand field strength is not affected significantly by the cyclohexane rings at the five-membered chelate rings. It has been widely observed that the values of the molar extinction coefficients of square planar Ni(II) complexes with saturated macrocyclic ligands are much lower in coordinating solvents than in nitromethane, a noncoordinating solvent.²⁵ This has been attributed to the fact that the complexes dissolve in the coordinating solvents (S) to give the equilibrium mixtures of the square planar [Ni(L)]²⁺ and octahedral [Ni(L)(S)₂]²⁺ species.²⁴⁻²⁷ In the case of [Ni(C)]²⁺, the extinction coefficient in water is rather similar to that measured in nitromethane and percent of the octahedral species calculated by the known method^{25,27} in aqueous solution at 25°C is only about 4%. The value is much lower than those reported for the Ni(II) complex with D(30%)²⁶ and E(66%).²⁴ It seems that the presence of the cyclohexane rings in the five-membered chelate rings causes more severe steric repulsion of the square planar with water molecules and makes the formation of the octahedral species more unfavorable. The spectra of Cu(II) complexes of B and C are also comparable to those reported for square planar Cu(II) complexes of various 14-membered tetraaza macrocyclic ligands.^{18,24} Maximum absorptions of the spectra of the Cu(II) complexes in water, acetonitrile, and N,N-dimethylformamide (DMF) are observed at some longer wavelengths than those in nitromethane. This suggests that the square planar Cu(II) complexes also coordinate the solvent molecules to form [Cu(L)(S)]²⁺ or [Cu(L)(S)₂]²⁺ species in the solutions.²⁸

¹H-NMR spectrum of [Ni(C)](PF₆)₂ measured in CD₃NO₂ solutions showed one doublet of the methyl protons at δ 1.75 ppm. For various square planar Ni(II) complexes of tetraaza macrocyclic ligands containing methyl groups at the carbon atoms of the six-membered chelate rings, it has been generally observed that axial methyl substituents occur ca. 1.7 ppm and equatorial methyls at ca. 1.3 ppm.²⁰⁻²⁴ The chemical shift for [Ni(C)]²⁺ strongly indicates that both of the two methyl groups in the complex are in axially oriented and the orientation is different from that for the free ligand, in which the two methyls are equatorially oriented as shown in above. It is clear that the conformation of the complex is different from that for the free ligand. In ¹³C-NMR spectrum of the complex, it has been observed that the pattern and position of the carbon peaks are quite similar to those for the free ligand. The ¹³C-NMR spectrum (Figure 2) of [Ni(B)](PF₆)₂ also shows ten peaks indicating one isomer with a center or a two fold axis of symmetry in the complexes. The most prominent feature in the spectrum is the peak of the imine groups, which appears at 192 ppm. Although the NMR spec-

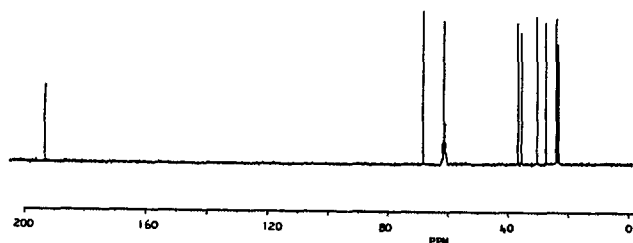


Figure 2. ¹³C-NMR spectrum of [Ni(B)](PF₆)₂ in CD₃NO₂ solution.

Table 2. Cyclic Voltammetric Data for the Ni(II) and Cu(II) Complexes^a

Complex	Potentials, V vs. SCE	
	[M(L)] ²⁺ → [M(L)] ³⁺	[M(L)] ²⁺ → [M(L)] ⁺
[Ni(B)](ClO ₄) ₂	+1.24(<i>i</i>) ^b	-12
[Ni(C)](ClO ₄) ₂	+1.08	-1.28
[Ni(D)] ²⁺ ^c	+0.92	-1.46
[Cu(B)](ClO ₄) ₂	+1.46	-0.49
[Cu(C)](ClO ₄) ₂	+1.41	-0.92(<i>i</i>) ^b
[Cu(D)] ²⁺ ^d	+1.35	-1.10

^a Measured in 0.1 M(n-Bu)₄NClO₄ acetonitrile solutions at 20°C.

^b *i* = irreversible. ^c Ref. 29. ^d Ref. 30.

tra of the ligand C and the Ni(II) complexes of B and C indicate that each compound is a diastereoisomer with a center or a two fold axis of symmetry, it is very difficult to determine the isomeric structures of the compounds from the NMR spectra.

Cyclic voltammograms of the Ni(II) and Cu(II) complexes in acetonitrile solutions exhibited two one-electron waves corresponding to M(II)/M(III) and M(II)/M(I) processes. Table 2 shows that both the oxidation and reduction potentials of Ni(II) and Cu(II) complexes of C are more anodic than those for the complexes of D^{29,30}, indicating that the complexes of C are easier to oxidize and more difficult to reduce. The more anodic potentials for the Ni(II) and Cu(II) complexes of B, compared with C, are resulted from the ligand unsaturation, which makes the oxidation of M(II) to M(III) more difficult and the reduction to M(I) easier.³¹

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Electrochemical Studies on Ion Recognition of Alkali Metal Cations by 18-crown-6 in Methanol

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Electrochemical studies of alkali metal cations (Na^+ , K^+ , Rb^+ , Cs^+) were performed in methanolic solutions of 18-crown-6 and tetrabutylammonium salts at dropping mercury electrodes (DME) and thin mercury film electrodes (TMFE). All the cations investigated were reduced reversibly at DME in the absence and presence of 18-crown-6, and in the latter the limiting currents were decreased and the reduction potentials shifted to the negative direction. The reduction potentials of the metal ions (0.2 mM) in the presence of the crown (10 mM) were -2.14 (Na^+), -2.26 (K^+), -2.20 (Rb^+) and -2.14 (Cs^+) V vs. SCE, respectively. The measured potentials were rationalized with ion recognition of the cations by the crown. Electroreduction at TMFE were highly irreversible. A new representation method of ion recognition is presented. In aqueous solutions, electroreduction of the alkali metal ions were characterized by adsorption.

Introduction

Recognition at the molecular level is a fundamental characteristic of enzyme catalysis, metal ion transport and information storage in biochemical systems.¹⁻³ There is a great deal of interest in elucidating mechanisms of molecular recognition by modeling host molecules that are highly selective in their binding to guest molecules or ions and by determining the thermodynamic stability constants in solutions and the crystal structures of host-guest complexes.^{4,5} A particular

class of host molecules studied extensively are the crown ethers. Extensive thermodynamic and kinetic data are compiled for cation-crown ether complexes by Izatt *et al.*⁶ Recent studies include theoretical evaluations of thermodynamic and kinetic aspects of Na^+ and K^+ -(18-crown-6) complexes.⁷⁻⁹

Although electrochemical methods can compensate for or excell other methods, *e.g.*, spectroscopic, calorimetric and potentiometric methods, in certain aspects to determine the thermodynamic and kinetic parameters on the complexation not many electrochemical investigations were made to cha-