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The effect of heterocyclic S,S'-ligands on the electrochemical properties of some cobalt(III) complexes in acid

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Abstract: Eight mixed-ligand cobalt(III) complexes with the macrocyclic amine 1,4,8,11-tetraazacyclotetradecane (cyclam) and a heterocyclic dithiocarbamate ($Rdtc^-$) *i.e.*, morpholine- (Morphdtc), thiomorpholine- (Timdtc), piperazine- (Pzdtc), *N*-methylpiperazine- (Mepzdtc), piperidine- (Pipdtc), 2-, 3- or 4-methylpiperidine- (2-, 3- and 4-Mepipdtc) carbodithionato-S,S ions, of the general formula $[Co(cyclam)Rdtc](ClO_4)_2$, were investigated in deoxygenated 0.1 M $HClO_4$ solutions. Cyclic voltammetry data at a glassy carbon (GC) electrode demonstrate a redox reaction of cobalt(III) from the complexes at potentials strongly influenced by the presence of different heterocyclic $Rdtc^-$ ligands. In this respect, the complexes were separated into two groups: the first, with a heteroatom O, S or N in the heterocyclic ring, and the second, with a methyl group on the piperidine ring of the $Rdtc^-$ ligand. Anodic polarization of an Fe electrode in the presence of the complexes shows their influence not only on the dissolution of iron but also on the hydrogen evolution reactions and on this basis complexes the complexes could be divided into the same two groups. It was found that the weaker the inhibiting effect of the free heterocyclic amines is, the significantly higher is the efficiency of the corresponding complexes.

Keywords: cobalt(III) complexes, azamacrocycles and dithiocarbamate, cyclic voltammetry, glassy carbon, iron, perchloric acid.

INTRODUCTION

The cobalt(III) ion forms a number of complexes with the tetraazamacrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) in the presence of two monodentate ligands,[1] favoring a planar arrangement of the macrocycle in the *trans* geometry. In fact the existence of both the *cis* and *trans* configuration[2] is possible, but with a high possibility of isomerization of the *cis* complexes in aqueous solutions.[3] However, a stable folded form of the cis geometry can be achieved by the use of

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some suitable exocyclic bidentate ligands.[4–7] Thus dithiocarbamates, as good chelating ligands, often have the capability to stabilize a metal ion in an unusually high oxidation state, coordinating through both of the sulfur atoms.[8,9] As a result, the formation of cobalt(III) mixed-ligand complexes with cyclam and dithiocarbamato ligands[5,6] can contribute to the acquisition of new information concerning the differences in behavior of bidentate ligands.

Mixed-ligand complexes can also be of interest from an electrochemical viewpoint because structural and electronic factors might affect the potentials of reactions such as hydrogen evolution and dissolution of metals in acids. As it is known, polar organic compounds containing sulfur, oxygen and nitrogen atoms, as well as their complexes could apparently inhibit these reactions.[10–14] A major influence on the bonding of an inhibitor to a metal surface and thus, protecting the surface from dissolution and hydrogen evolution depends on the molecular structure of the inibitor, mainly on the presence of functional groups(s). For example, the protection of steel from dissolution in sulfuric acid was found to be more effective in the presence of some dithiocarbamate derivatives which slow down the rate of hydrogen evolution on the metal, acting as mixed-type of inhibitors.[15]

Recently, eight cobalt(III) complexes of the general formula [Co(cyclam) Rdtc]$(ClO_4)_2$, [Rdtc$^-$ = morpholine- (Morphdtc), thiomorpholine- (Timdtc), piperazine- (Pzdtc), *N*-methylpiperazine- (Mepzdtc), piperidine- (Pipdtc), 2-, 3- or 4-methylpiperidine- (2-, 3- and 4-Mepipdtc) dithiocarbamates] were characterized.[5–7] The electrochemical examination of these substances in aqueous and non-aqueous solutions showed the influence of the bidentate heterocyclic S,S'-ligand on the electrochemical behavior of the complexes.[16] Preliminary results of the [Co(cyclam)Pzdtc]$(ClO_4)_2$ complex demonstrate its inhibiting influence on the dissolution of iron in acidic solutions.

The aim of this work was to examine the behavior of a series of [Co(cyclam) Rdtc(*1–8*)]$(ClO_4)_2$ complexes (Fig. 1) in oxygen-free solutions of perchloric acid. Using GC and Fe electrodes, the effect of these compounds was followed through their influence on redox-, hydrogen evolution and metal dissolution reactions.

EXPERIMENTAL

The electrochemical stability of the [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$ complexes was examined by cyclic voltammetry (CV) at a glassy carbon electrode in 0.1 M $HClO_4$ solution. The glassy carbon (GC) disc electrode (Sigradur-Sigri Elektrographite, GmbH, Germany) was mechanically treated with emery paper of decreasing grain size followed by polishing with alumina (0.5 μm particle size) prior to each experiment. The electrode was cleaned in 18 MΩ water in an ultra sonic bath and was first examined in the basic electrolyte by cyclic voltammetry before the substance was added to the solution. Cyclic voltammetry was performed at a sweep rate of 100 mV/s. The potential range examined was between and –1.0 V to 1.2 V. The counter electrode was a platinum wire. A saturated calomel electrode (SCE) was used as the reference and all the potentials are given *versus* the SCE electrode.

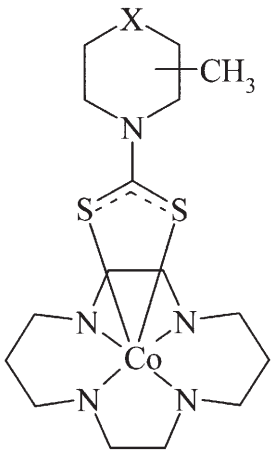


Fig. 1. The structure of the complexes [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$: (*1*) Morphdtc X=O; (*2*) Timdtc X=S; (*3*) Pzdtc X=NH; (*4*) Mepzdtc X=N-CH_3; (*5*) Pipdtc X=CH_2; (*6*) 2-Mepipdtc X=CH_2, *ortho*-CH_3; (*7*) 3-Mepipdtc X=CH_2, *meta*-CH_3; (*8*) 4-Mepipdtc X=CH_2, *para*-CH_3 group.

All the complexes [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$, as well as the corresponding heterocyclic amines, *i.e.*, Morph, Tim, Pz, Mepz, Pip, 2-Mepip, 3-Mepip or 4-Mepip, were examined as possible inhibitors of iron corrosion at concentations of 10^{-5} and 10^{-4} M in 0.1 M $HClO_4$ solution.

An iron rod (Jonhson Matthew, Puratronic 99.99 %) was mechanically buffed with emery paper of decreasing grain size. The rod was sealed in a Teflon holder by pressure and an epoxy resin so that only the working surface was exposed to the solution. The counter electrode was a Pt wire and the reference electrode was a double junction SCE. The iron electrode was polarized between – 0.65 V to – 0.2 V *vs*, SCE at a sweep rate of 5 mV/s. The electrode was immersed in deaerated solutions to be examined for one hour before starting the measurements.

The structures of the complex [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$ studied are presented in Fig. 1. All the investigated compounds were obtained using the syntheses described elsewhere.[5,6] They were added to the 0.1 M $HClO_4$ (Fisher Scientific) without pretreatment. The solutions were prepared from analytical grade reagents using 18 MΩ H_2O and were maintained oxygen-free by purging with nitrogen. All the experiments were performed at room temperature in a three-electrode compartment electrochemical cell with the electronic equipment consisting of a Pine Instrument, model RDE4 Potentiostat and a Philips model 8033 X-Y recorder.

RESULTS AND DISCUSSION

Cyclic voltammetry

A previous examination of the series of eight [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$ complexes in $NaClO_4$ solution demonstrated that coordination to cobalt(III) stabilizes both the cyclam and the $Rdtc^-$ ligands.[16] The cobalt(III) ion itself undergoes redox reactions from the complexes at potentials influenced by the presence of the different heterocyclic dithio-ligands.[16]

The cyclic voltammograms recorded, Fig. 2 (representative example), are characteristic and similar for all of the complexes with a redox peak-pair in the negative potential region and a less pronounced peak-pair in the positive potential region. The peaks in the positive region are characteristic of this electrode material in acidic solutions *i.e.*, they correspond to the glassy carbon electrode itself.[17] The redox peak-pair in the negative potential region has an anodic peak at – 0.68 V and a cathodic one at – 0.74 V *vs.* SCE for the complexes [Co(cyclam)Rdtc(*1–4*)]$(ClO_4)_2$,

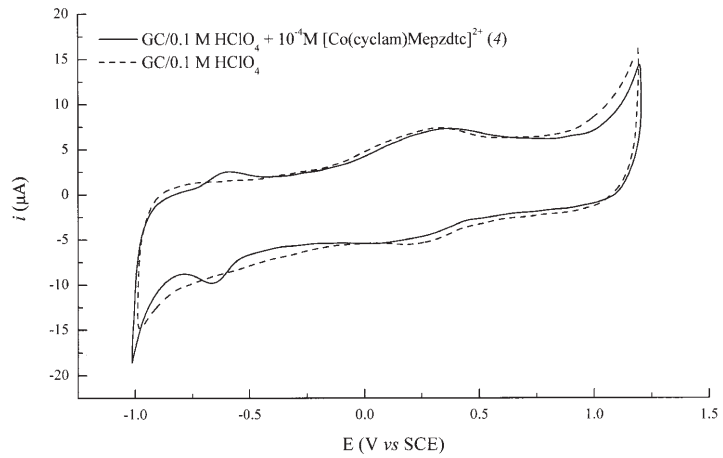


Fig. 2. Cyclic voltammograms at a GC electrode in 0.1 M $HClO_4$ and in the presence of 10^{-1} M [Co(cyclam)Mepzdtc]$(ClO_4)_2$ complex; sweep rate 100 mV/s.

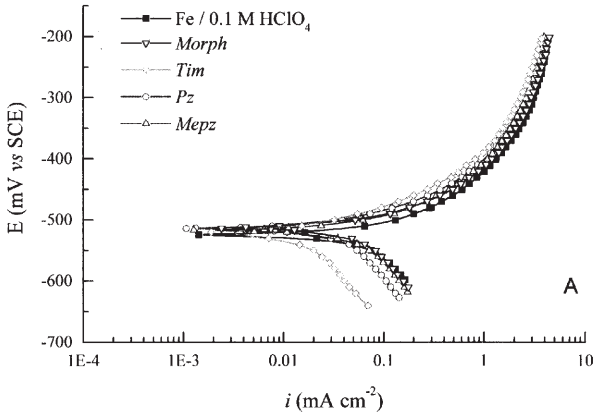
and at – 0.72 V and – 0.78 V *vs.* SCE for the complexes [Co(cyclam)Rdtc(*5–8*)]$(ClO_4)_2$. Thus, this pair of redox peaks belongs to the Co^{III}/Co^{II} couple and marks the redox reaction of central metal ion from the complex. The potential values of the peak-to-peak maximum differ by 60 mV, indicating a one-electron exchange reaction. Furthermore, the potential values do not depend on the pH of the solution, being the same as in $NaClO_4$ solution,[16] but depend on the structural nature of the chelate-S,S' ligands.

Based on the potentials of the redox pair, the complexes can be divided into two groups: the first group, containing the complexes with a heteroatom O, S or N in the ring when the redox reaction of the Co^{III}/Co^{II} ions occurs at less negative potentials and the second group, encompassing the complexes with a methyl group on the piperidine ring when the redox reaction occurs at more negative potential values. The electron-releasing and electron-withdrawing effects of the methyl group and the polar atom, respectively, affect the electron density variation throughout the delocalized bonds of the $>NCS_2$ group of the dithio-ligands ($Rdtc^-$). This, consequently, influences the potential shift of the cobalt redox reaction in the same range for the first, [Co(cyclam)Rdtc(*1–4*)]$(ClO_4)_2$ and second, [Co(cyclam)Rdtc (*5–8*)]$(ClO_4)_2$ group of complexes.

Moreover, the cyclic voltammetry data indicate an influence of the complexes on hydrogen evolution in acid solution by increasing the reaction current to some extent (Fig. 2). The higher current in the case of the piperidine derivatives group of complexes, [Co(cyclam)Rdtc(*5–8*)]$(ClO_4)_2$ exhibits a larger influence on the cathodic reaction.

Anodic polarization

Preliminary results[16] showed that the reaction on an iron electrode in deoxygenated 0.1 M $HClO_4$ solution is inhibited by the presence of the [Co(cyclam)



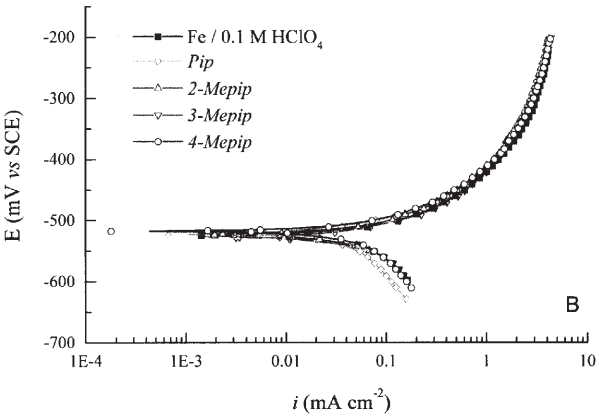


Fig. 3. Polarization curves for iron in oxygen-free 0.1 M $HClO_4$ solutions and in the presence of 10^{-4} M heterocyclic amines; sweep rate 5 mV/s. A) First group of the amines; B) Second group of the amines.

Pzdtc]$(ClO_4)_2$ complex to some extent, more than by the amine piperazine itself. The corresponding piperazinedithiocarbamate (Pzdtc), however, enhanced both reactions, the dissolution of iron and the evolution of hydrogen, probably due to the accelerating effect of the CS_2 produced after decomposition of $Rdtc^-$ in acid.[18] In this study, all eight heterocyclic amines and the corresponding complexes were investigated in 10^{-5} M and 10^{-4} M concentrations of $HClO_4$ and the results obtained are presented in Tables I and II, as well as in Figs. 3 and 4, respectively.

Generally, these acid concentrations are not sufficient to reduce the acid dissolution of iron to a great extent, but they are enough to propose and distinguish the behavior between both amines and related complexes, separated as: the first group of amines and the related complexes [Co(cyclam)Rdtc(*1–4*)]$(ClO_4)_2$, and the second group of amines and the corresponding complexes [Co(cyclam)Rdtc(*5–8*)] $(ClO_4)_2$, based on small but characteristic structural differences.

The results presented in Table I show that an amine concentration of 10^{-5} M is too low for any significant inhibiting action of the anodic reaction. Amines (*1–8*),

however, have some negligible influence on the hydrogen evolution (cathodic reaction). A more pronounced effect could be observed for the first (*1–4*) than for the second (*5–8*) group.

TABLE I. Electrochemical data for iron polarization in 0.1 M $HClO_4$ solution in the presence of the heterocyclic amines

Compound	Conc./M	i_c/mA cm^{-2}	i_a/mA cm^{-2}	b_c/mV dec^{-1}	b_a/mV dec^{-1}
Free acid	0.1	0.114	0.607	130	80
Morph	10^{-5}	0.110	0.581	160	80
	10^{-4}	0.098	0.489	160	80
Tim	10^{-5}	0.112	0.577	130	80
	10^{-4}	0.029	0.274	160	80
Pz	10^{-5}	0.092	0.479	160	80
	10^{-4}	0.073	0.366	160	80
Mepz	10^{-5}	0.099	0.539	160	80
	10^{-4}	0.072	0.452	160	80
Pip	10^{-5}	0.088	0.563	130	80
	10^{-4}	0.076	0.496	130	80
2-Mepip	10^{-5}	0.110	0.602	130	80
	10^{-4}	0.108	0.508	130	80
3-Mepip	10^{-5}	0.113	0.606	130	80
	10^{-4}	0.082	0.569	130	80
4-Mepip	10^{-5}	0.109	0.539	130	80
	10^{-4}	0.106	0.478	130	80

i_c – current density for hydrogen evolution at –570 V *vs.* SCE; i_a – current density for dissolution of iron at –450 mV *vs.* SCE; b_c and b_a – cathodic and anodic slope of the Tafel lines

The amines at a higher concentration (10^{-4} M) have a somewhat greater influence on both electrochemical reactions. As can be seen from Fig. 3A, the cathodic and anodic *E*/*i* curves are shifted to lower current values compared with those for unprotected iron. The inhibitory influence of an amine with a heteroatom on the cathodic reaction is still larger (Table I), and the inhibiton effect on both the anodic and cathodic reaction follows the order Tim > Pz > Mepz > Morph. It is not surprising for sulfur compounds to have a greater inhibition erffectiveness than nitrogen and oxygen compounds, probably because of the higher polarizability of sulfur.[19] Amines of the piperidine group (at 10^{-4} M) have a small influence on the dissolution of iron in acid and on the hydrogen evolution reaction (Fig. 3B, Table I). Only in the case of piperidine is the cathodic reaction current shifted to a lower value. In both concentrations, amines from the second group (*5–8*) do not affect the Tafel slopes (b_c and b_a) which are the same as in free acid. The amines from the first group (*1–4*), however, influence the cathodic reaction with some deviations of the Tafel slope.

On the other hand, all the [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$, complexes exhibit a stronger influence on the dissolution of iron at both employed concentrations. At a concentration of 10^{-5} M, the cobalt complexes demonstrated a smaller influence on the anodic than on the cathodic reaction (Table II). The largest current decrease of the hydrogen evolution reaction (Table II) occurred with the complex [Co(cyclam)Rdtc(*3*)] $(ClO_4)_2$ from the first group, followed by the complexes (*4*) and (*1*), and finally, complex (*2*) has the smallest influence. In the case of the second group (Table II), the largest shift of the current density was shown by the complex [Co(cyclam)Rdtc(*5*)]$(ClO_4)_2$, and the complex (*8*) with a *para*-CH_3 group, has the smallest effect.

TABLE II. Electrochemical data for iron polarization in 0.1 M $HClO_4$ solution in the presence of the complexes [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$

Compound	Conc. M	i_c/mA cm^{-2}	i_a/mA cm^{-2}	b_c/mV dec^{-1}	b_a/mV dec^{-1}
Free acid	0.1	0.114	0.607	130	80
Complex (*1*)*	10^{-5}	0.084	0.409	160	80
	10^{-4}	0.055	0.362	110	10
Complex (*2*)	10^{-5}	0.112	0.424	160	80
	10^{-4}	0.088	0.200	130	80
Complex (*3*)	10^{-5}	0.059	0.439	160	80
	10^{-4}	0.040	0.227	160	80
Complex (*4*)	10^{-5}	0.093	0.520	160	80
	10^{-4}	0.091	0.348	130	100
Complex (*5*)	10^{-5}	0.066	0.453	130	80
	10^{-4}	0.033	0.201	130	80
Complex (*6*)	10^{-5}	0.088	0.345	130	80
	10^{-4}	0.083	0.224	130	80
Complex (*7*)	10^{-5}	0.096	0.533	130	80
	10^{-4}	0.013	0.293	130	80
Complex (*8*)	10^{-5}	0.109	0.539	130	80
	10^{-4}	0.062	0.293	130	80

i_c – current density for hydrogen evolution at –570 V *vs.* SCE; i_a – current density for dissolution of iron at –450 mV *vs.* SCE; b_c and b_a – cathodic and anodic slope of the Tafel lines; * Numbers in parentheses correspond to the $Rdtc^-$ ligands from the complexes of the general formula [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$.

The influence of the complexes on both the anodic and the cathodic reaction is more pronounced at the higher concentration (10^{-4} M). The polarization curves for iron in the presence of the complexes are given in Fig. 4 and the related electrochemical data in Table II. The Tafel curves, Fig. 4A, indicate the influence of the first group of complexes [Co(cyclam)Rdtc(*1–4*)]$(ClO_4)_2$ on both reactions to the same extent, but with different magnitudes of the displacement of the Tafel plots compared with free acid (Table II). On the other hand, as can be seen from Fig. 4B

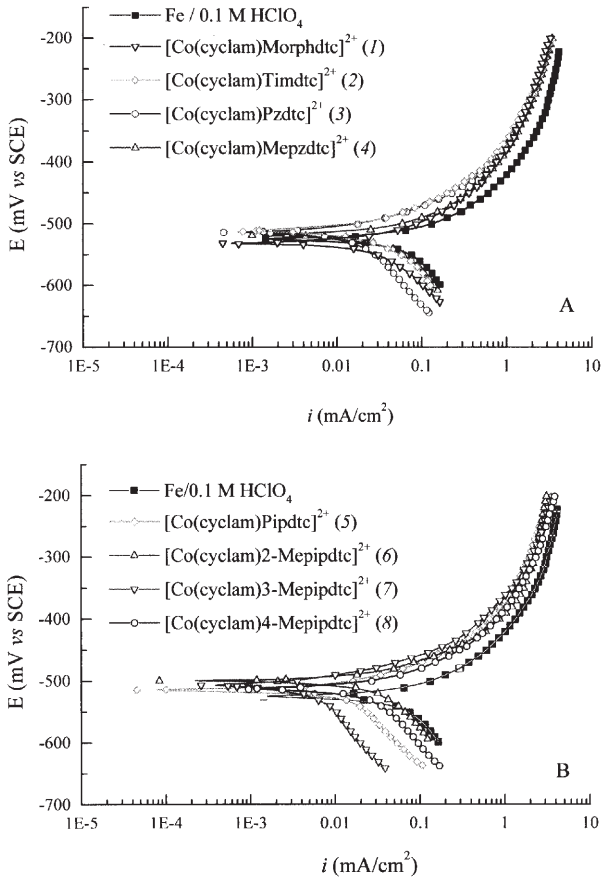


Fig. 4. Polarization curves for iron in oxygen-free 0.1 M $HClO_4$ solutions and in the presence of 10^{-4} M [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$ complexes; sweep rate 5 mV/s. A) First group of the complexes (*1–4*); B) Second group of the complexes (*5–8*).

and Table II, the complexes [Co(cyclam)Rdtc(*5–8*)]$(ClO_4)_2$ affect both the anodic and the cathodic reaction with a somewhat more pronounced effect on the cathodic one. Both Tafel lines are shifted parallel to the one for the free acid.

A change of the slope (b_a and b_c) is a sign of a change in the reaction mechanism. According to Grigory[20] and Antropov,[21] hydrogen evolution on iron in acidic solutions proceeds with the recombination of adsorbed hydrogen atoms forming hydrogen molecules as the rate-determining step. The addition of inhibitors retards the rate of hydrogen evolution by affecting the reaction mechanism, as indicated by the change in the Tafel slope.[15] In the presence of such compounds, the retarded formation of adsorbed hydrogen atoms seems to control the rate of the overall hydrogen evolution reaction.[22] Although the [Co(cyclam)Rdtc(*1–8*)]$(ClO_4)_2$ complexes exhibit a similar influence on the corrosion of iron in acidic media, more detailed examinations are needed to discuss the change of the reaction mechanism.

Correlation with spectroscopy data

On the basis of the obtained results, all the complexes demonstrate a stronger effect on the hydrogen evolution reaction than on the oxidation of iron. It seems that the inhibition of iron dissolution, in general, is greater in the presence of the second group of piperidine complexes [Co(cyclam)Rdtc(*5–8*)]$(ClO_4)_2$ than in the presence of those of the first group [Co(cyclam)Rdtc(*1–4*)]$(ClO_4)_2$ (Table II). The corresponding amines exhibit opposite effects: the first group of amines (*1–4*) with a heteroatom in the cyclic ring affects iron dissolution to a greater extent. Also, it appears that the smaller the inhibiting effect of the free amine is, the greater is the inhibiting effect of the corresponding complex on the corrosion of iron. Some of the findings could be explained using previously obtained spectroscopic IR and NMR data of the complexes.[5,7]

Those results show a shift in the frequencies of the partially delocalized >C ··· N bond in IR spectra of the ligating $>NCS_2$ group. The complexes of the first group with a heteroatom, O, S or N, in the cyclic ring have ν(CN) values at higher energies than the piperidines. In this respect, the reduced electron density at the $>NCS_2$ ligating group, consequently, produces a weaker Co-Rdtc$^-$ coordination bond in comparison with the complexes with an electron-releasing substituents. The influence of the is also evidenced in the resonances of the $>NCS_2$ group in the ^{13}C-NMR spectra. The deshielding effect of these resonances is an indication of a stronger metal–ligand bond of the corresponding Rdtc$^-$ ligand.[22] These are greater in case of piperidine and its methyl-derivatives than those of the heteroatom piperidines.

In general, the ability to inhibit acid corrosion can be correlated with the degree of adsorption of the inhibitor compound. Amine inhibition derives from their electron-donor properties, which are better for the methylpiperidines than for the heteroatom molecules. The corresponding chemisorption of piperidinium cations can occur by the sharing of electrons between nitrogen and iron or by the displacement of water molecules from the metal surface.[23]

The complexes could be bonded to the metal surface through a coordination type of bond formed due to electron transfer from the inhibitor molecule to the metal.[15] The coordination of a Rdtc$^-$ ligand with a higher density towards the $>NCS_2$ group leads to a stronger Co-ligand bond. The stronger the metal-ligand bond in a complex is, the higher is the electron density on the adsorption part of the molecule and thus the higher is the inhibition. Therefore, a greater adsorption and inhibition efficiency is to be expected for those compounds with a greater electron density at the adsorption center.

CONSLUSION

Based on the peak potentials of the redox pair from cyclic voltammetry data, two groups of the complexes can be distinguished: first, the complexes with a

heteroatom in the ring with a redox reaction of the Co^{III}/Co^{II} ions that occurs at less negative potentials than for the second group of complexes with a methyl substituent on the piperidine ring.

Anodic polarization of an iron electrode in perchloric acid in the presence of the examined complexes, as well as the corresponding amines indicates their possible inhibiting action on iron dissolution and hydrogen evolution. The weaker is the inhibiting effect of a free amine, the stronger is the effect of the corresponding complex. The stronger metal-ligand bond in the complex leads to a higher electron density on the adsorption part of the molecule and, thus, to greater inhibition.

Further examinations of the inhibiting properties and effectiveness of the here-described molecules should be done in detail by different electrochemical methods.

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ИЗВОД

УТИЦАЈ ХЕТЕРОЦИКЛИЧНИХ S,S'-ЛИГАНАДА НА ЕЛЕКТРОХЕМИЈСКЕ ОСОБИНЕ НЕКИХ КОБАЛТ(III) КОМПЛЕКСА У КИСЕЛОЈ СРЕДИНИ

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Осам мешовито-лигандних комплекса кобалта(III) са макроцикличним амином 1,4,8,11-тетраазациклотетрадеканом (cyclam) и хетероцикличним дитиокарбаматима ($Rdtc^-$) т.ј., морфолин- (Morphdtc), тиоморфолин- (Timdtc), пиперазин- (Pzdtc), *N*-метилпиперазин- (Mepzdtc), пиперидин- (Pipdtc), 2-, 3- или 4-метилпиперидин- (2-, 3- и 4-Mepipdtc) карбодитионато-S,S јонима, опште формуле $[Co(cyclam)Rdtc)](ClO_4)_2$, испитано је у 0,1 M $HClO_4$ раствору на електроди од стакластог угљеника и гвожђа. Циклична волтаметрија на електроди од стакластог угљеника показала је да долази до редокс реакције кобалт(III) јона из комплекса. Различити хетероциклични $Rdtc^-$ лиганди утичу на вредност потенцијала ове редокс реакције. На основу ових вредности комплекси се могу поделити у две групе: једну са хетероатомом у хетероцикличном прстену и другу са метил-групом на пиперидинском прстену $Rdtc^-$ лиганда. Анодна поларизација гвожђа у присуству комплекса показала је њихов утицај не само на реакцију растварања метала већ и на реакцију издвајања водоника. Резултати су показали да што је слабији инхибиторски ефекат хетероцикличног амина то је већи утицај одговарајућег комплекса.

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