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Molecular structure in correlation with electrochemical properties of mixed-ligand cobalt(III) complexes

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Abstract: Four mixed-ligand cobalt(III) complexes (**1–4**) of the general formula [Co(Rdte)cyclam](ClO₄)₂ and [Co(Rac)cyclam](ClO₄)₂ (cyclam = 1,4,8,11-tetraazacyclotetradecane; Rdte = thiomorpholine-(Timdte) or 2-methylpiperidine-(2-Mepipdte) dithiocarbamates; Rac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (Hfac) or 2,2,6,6-tetramethyl-3,5-heptanedionato (Tmhd), respectively) were electrochemically examined on a glassy carbon and an iron electrode in perchloric acid solution. The obtained results showed the influence of these complexes on hydrogen evolution, the oxygen reduction reaction and iron dissolution. The exhibited effects of the complexes on these reactions depend on structure related to the bidentate dithiocarbamate or β -diketonato ligand. The electrochemical properties of the complexes were correlated with molecular structure and parameters derived from spectral analysis and molecular modeling.

Keywords: cobalt(III) complexes; cyclam; dithiocarbamate ligands; β -diketonato ligands; MOT.

INTRODUCTION

In many respects, tetraazamacrocycles have attracted considerable attention as biomimetic and catalytic systems.¹ They can sequester many transition metal ions to form complexes which exhibit various chemical and physical properties, such as molecular recognition of DNA and RNA,^{2,3} electro- or photo-activation of CO₂,^{4,5} and can act as metalloenzyme models,^{6,7} depending on the coordination properties of the pendant donor group. Furthermore, among these series, some complexes have found application in medical and pharmaceutical fields as contrast-enhancing agents.^{9–11}

The macrocyclic [14]ane-N₄ ligand cyclam is prone to coordinate the metal in a pseudo planar geometry due to its flexibility, which induces favored con-

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figurations.^{12–15} However, the topology of the bidentate extracyclic ligand directly influences the size of the cavity and the coordination parameters. This paper is focused on a model study of previously synthesized cobalt(III)–cyclam complexes containing dithiocarbamato¹⁴ or β -diketonato ligands.¹⁵ There is, indeed, an interest in elucidating the role played by dithiocarbamato as well as β -diketonato ligands, since similar complexes exhibit certain electrochemical properties.^{12,16,19} It is interesting to point out the relation between structural parameters and the results obtained from electrochemical measurements, *i.e.*, electrocatalysis and inhibition studies. In this respect, the ability to predict and hence to interpret principal modes of interactions of structurally diverse compounds will help to develop a parallel route to analogues.

EXPERIMENTAL

All the employed chemicals were commercial products of analytical reagent grade. The corresponding cobalt(III)–cyclam complexes were obtained according to the procedures described in the literature.^{14,15}

The complexes were examined on a glassy carbon (GC) and an iron electrode in 0.10 M HClO₄ and 0.10 M NaClO₄ solution. A GC disc (Sigardur-Sigri Electrographite, GmbH, Germany) was used as the working electrode for the characterization of the complexes. The electrode surface was mechanically treated with emery paper of decreasing grain size, polished with alumina (0.5 μ m particle size) and cleaned in double-distilled deionized water in an ultrasonic bath. The GC electrode was tested in blank electrolyte by cyclic voltammetry (CV) before the substance was added to the solution. The reduction of oxygen in the presence of the [Co(Rdtc)cyclam](ClO₄)₂ complexes was examined in 0.10 M HClO₄ saturated with O₂ at a rotating GC electrode at a sweep rate of 5.0 mV s⁻¹ and a rotation rate 900 rpm.

The iron rod electrode (Puratronic 99.99 %, Johnson Matthey Company) used for the corrosion tests was mechanically finished with emery paper. The electrode was immersed in electrolyte solution for 1 h before commencing the measurements. The inhibiting effect of the complexes was studied by potentiodynamic measurements in an oxygenated atmosphere. The measurements were performed using a Potentiostat/Galvanostat/ZRA, Gamry Instruments, and data were processed using Elchem Analyst software. The current–potential curves were obtained by changing the electrode potential automatically from –250 to 250 mV_{SCE} at a scan rate of 1.0 mV s⁻¹.

The solutions were prepared from analytical grade reagents using double-distilled deionized water. All of the experiments were performed at room temperature in a three-electrode compartment electrochemical cell. The counter electrode was a Pt wire and saturated calomel electrode (SCE) was used as the reference. All potentials are given *vs.* SCE.

For molecular modeling, a quantum-mechanical Hyperchem program was used (Hypercube Inc., Version 7). The molecular orbital (MO) calculations were based on the semi-empirical self-consistent field (SCF) method. A full optimization of all geometrical variables without any symmetry constraint was performed using the Zindo/1 method.

RESULTS AND DISCUSSION

The analytical results confirmed the proposed compositions of the complexes.

[Co(Timdtc)cyclam](ClO₄)₂ (**I**). Anal. Calcd. (%) for C₁₅H₃₂Cl₂CoN₅O₈S₃ (636.47): C, 28.66; H, 5.27; N, 10.62. Found: C, 28.31; H, 5.07; N, 11.00.

[Co(2-Mepipdte)cyclam](ClO₄)₂ (2). Anal. Calcd. (%) for C₁₇H₃₆Cl₂CoN₅O₈S₂ (632.46): C, 32.17; H, 5.80; N, 11.22. Found: C, 32.28; H, 5.74; N, 11.07.

[Co(Hfac)cyclam](ClO₄)₂ (3). Anal. Calcd. (%) for C₁₅H₂₅Cl₂CoN₄O₁₀F₆ (665.20): C, 27.08; H, 3.79; N, 8.42. Found: C, 27.33; H, 3.93; N, 8.82.

[Co(Tmhd)cyclam](ClO₄)₂ (4). Anal. Calcd. (%) for C₂₁H₄₃Cl₂CoN₄O₁₀ (641.51): C, 39.32; H, 6.76; N, 8.73. Found: C, 39.36; H, 6.89; N, 8.95.

Dithiocarbamato-Co(III)cyclam complexes

The [Co(Rdte)cyclam](ClO₄)₂ complexes were electrochemically characterized on a GC electrode in 0.10 M NaClO₄. A 0.10 M perchloric acid solution was used to study their possible effects on oxygen reduction and corrosion inhibition. The cyclic voltammograms recorded for the complexes in 0.10 M HClO₄ are presented in Fig. 1. The recorded voltammograms are similar for both complexes with a redox peak pair in the negative potential region and a less pronounced peak pair in the positive potential region. The redox pair in the positive region is a characteristic of the electrode material itself in acidic solutions, *i.e.*, it corresponds to glassy carbon.²⁰ The potential values of the redox pair in the negative region do not depend on pH, being the same in NaClO₄ and HClO₄ solution. This pair of peaks was recorded only on the CVs of the complexes and was not present on the voltammograms of either of the ligands.¹⁶ Thus, this pair of redox peaks marks the redox reaction of the central metal ion in the complex, *i.e.*, it belongs to the Co(III)/Co(II) couple. As can be seen from Fig. 1, the potential values depend on the structural nature of the chelate-*S,S'* ligands, being more negative in the presence of [Co(2-Mepip)cyclam](ClO₄)₂. The CV data also indicate the influence of the complexes on hydrogen evolution in perchloric acid, by shifting its potential cathodically (Fig. 1). The higher potential shift in case of the [Co(2-Mepipdte)cyclam](ClO₄)₂ complex shows its larger influence on the cathodic reaction.

Preliminary examinations of oxygen reduction in the presence of the dithiocarbamato Co(III)–cyclam complexes showed a possible catalytic effect on the reaction in acidic media (Fig. 2). The obtained results illustrate that the complexes influence oxygen reduction by shifting the potential in the anodic direction. In this case, a larger effect was observed with the [Co(Timdte)cyclam](ClO₄)₂ complex.

Corrosion tests on an iron electrode in the presence of either of the dithiocarbamato complexes showed their inhibiting effect in acidic solution, influencing both the anodic and cathodic reaction. Both complexes demonstrate a strong effect on the hydrogen evolution reaction. The polarization curves (Fig. 3) indicate the influence of the [Co(Timdte)cyclam](ClO₄)₂ complex on the anodic reaction in comparison with the free acid, although, the [Co(2-Mepipdte)cyclam](ClO₄)₂ complex showed a greater cathodic protection and a higher inhibitor efficiency. Thus, the complex that suppresses hydrogen evolution more was found to be a better corrosion inhibitor.

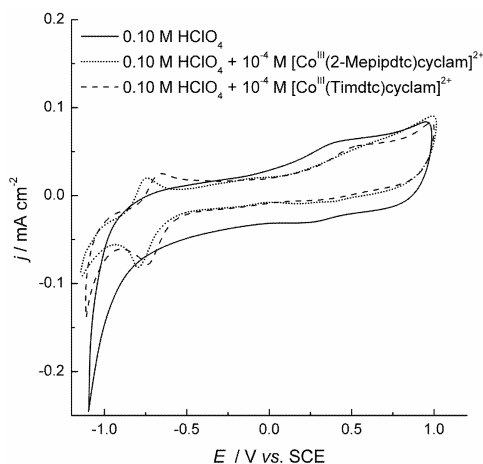


Fig. 1. Cyclic voltammograms at a GC electrode in 0.10 M HClO₄ without and with 10⁻⁴ M [CoIII(Rdtc)cyclam](ClO₄)₂ complexes (sweep rate: 50 mV s⁻¹).

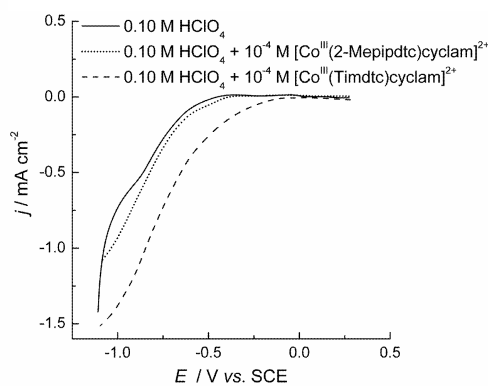


Fig. 2. Oxygen reduction curves at a GC electrode in 0.10 M HClO₄ without and with 10⁻⁴ M [CoIII(Rdtc)cyclam](ClO₄)₂ complexes (sweep rate: 5.0 mV s⁻¹, $\omega = 900$ rpm).

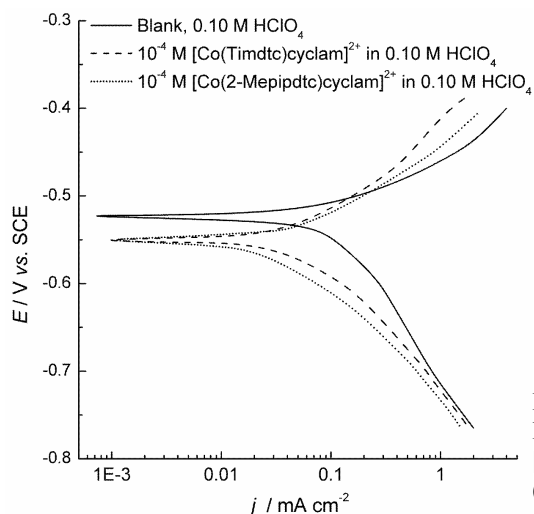


Fig. 3. Polarization curves for iron in 0.10 M HClO₄ and in the presence of 10⁻⁴ M [Co(III)(Rdtc)cyclam](ClO₄)₂ complexes (sweep rate: 1.0 mV s⁻¹).

The position of the methyl group on the piperidine ring and/or the presence of a heteroatom in the ring is reflected in a shift of the C=N bond frequencies in the part of the Rdtc⁻ ligand in the IR spectra.^{13,14} Selected IR spectral data of the examined complexes are given in Table I. The data show that the $\nu(\text{CN})$ in the [Co(2-Mepipdtc)cyclam](ClO₄)₂ complex was shifted to lower energies due to the positive inductive effect of the methyl group in the complex. On the other hand, the heteroatom in the [Co(Timdtc)cyclam](ClO₄)₂ complex influenced the C=N bond frequency, $\nu(\text{C=N})$, by shifting it to higher energies. Electronic effects, as noticed, consequently affect the potential shift of the cobalt re-

dox reaction and electrochemical reactions. Accordingly, with a stronger CN bond, the potentials will be shifted to more negative values.

TABLE I. Selected IR spectral data (cm^{-1}) of the $[\text{Co}(\text{Rdtc})\text{cyclam}](\text{ClO}_4)_2$ complexes

Complex	$\nu(\text{C} \equiv \text{N})$	$\nu(\text{C} = \text{S})$
$[\text{Co}(\text{Timdtc})\text{cyclam}](\text{ClO}_4)_2$ (1)	1528 _{vs} ^a	1013 _s
$[\text{Co}(2\text{-Mepipdtc})\text{cyclam}](\text{ClO}_4)_2$ (2)	1438 _{vs}	954 _s

^a_{vs}: Very strong; _s: strong

The chemical shifts in ^{13}C -NMR spectra of the $>\text{NCS}_2$ group on the Rdtc^- ligands showed slight differences between the complexes in the same order as was established from the electrochemical data. The deshielding effect on these resonances is an indication of the stronger metal–ligand bond²¹ and greater electron density of the ligating group. As the effect was greater for the $[\text{Co}(2\text{-Mepipdtc})\text{cyclam}]^{2+}$ than for the $[\text{Co}(\text{Timdtc})\text{cyclam}]^{2+}$ complex, its inhibiting effect on iron corrosion was also bigger. In general, the adsorption of the complexes on the metal surface is most likely realized through a coordinate type of bond formed due to electron transfer from the inhibitor molecule to the metal. The coordinated Rdtc^- ligand with a higher density towards the $>\text{NCS}_2$ group results in a stronger Co–ligand bond. The stronger metal–ligand bond in the complex leads to a higher electron density on the adsorption part of the molecule and, thus, greater inhibition. Therefore, a greater adsorption and larger inhibition efficiency should be expected for those compounds with a greater electron density at the adsorption centre.

Molecular modeling calculations were used to correlate the structural properties of the complex species and their inhibition efficiency.^{17,18} According to the known crystal data,^{12,22} the complex molecules are in a distorted octahedron geometry with the typical conformational flexibility of a large cyclic ring with a minimum steric constrains and with significant delocalization along the $>\text{NCS}_2$ group of the Rdtc^- ligand. The Zindo/1 optimized structure for the $[\text{Co}(\text{Timdtc})\text{cyclam}](\text{ClO}_4)_2$ complex is shown in Fig. 4.

The HOMO (highest occupied MO) energy is often associated with the electron donating ability of a molecule. The presence of a methyl group on the heterocyclic ring decreases the ionization potential ($I = -E_{\text{HOMO}}$) and the energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$; E_{LUMO} is the lowest unoccupied MO), which is reflected in a stronger chemisorption bond and perhaps a greater inhibitor efficiency. In addition, the presence of a methyl group on the Rdtc^- ligand intensifies the ligand field strengths and amine basicities, and thus affects the inhibitor efficiency. These facts can be used to show that small differences in the inhibiting behavior of the complexes are a consequence of their electronic and structural effects, together with conjugation of the double bonds through the $>\text{NCS}_2$ group of the dithiocarbamate ligand.

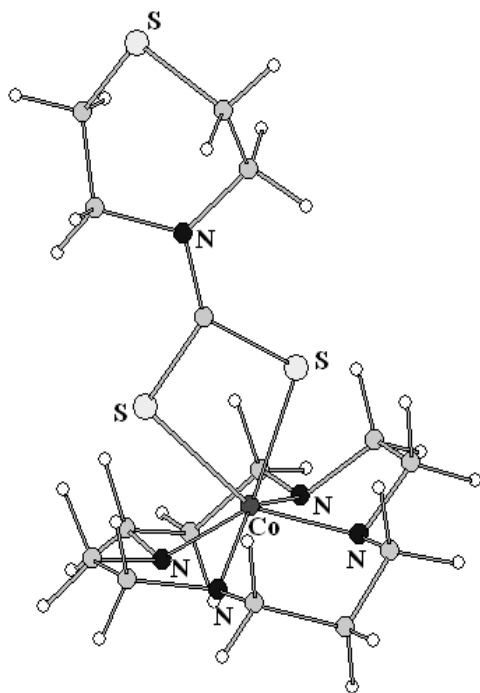


Fig. 4. Zindo/1 optimized structure for the complex $[\text{Co}(\text{Timdtc})\text{cyclam}]^{2+}$.

β -Diketonato-Co(III)cyclam complexes

The CVs of the $[\text{Co}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes examined at a GC electrode in aqueous NaClO_4 solution are presented in Fig. 5. A single quasi-reversible redox wave in the range -250 to -400 mV, depending on the diketonato Rac^- ligand, with a peak-to-peak separation of about 100 mV, was recorded on both voltammograms. This pair of peaks should present the Co(III)/Co(II) redox reaction. Such a redox pair, as previously found, characterizes $[\text{Co}(\text{Rdtc})\text{cyclam}]^{2+}$ complexes (at about -700 mV) as well as the $[\text{Co}(\text{ox})\text{cyclam}]^+$ complex (at about -400 mV).¹² Therefore, the anodic shift of the redox potential, in the order of the bidentates $\text{Rac}^- > \text{ox}^{2-} > \text{Rdtc}^-$, is most likely related to the σ - and π -ligand donor properties.

The CVs in aqueous NaClO_4 solutions (Fig. 5) show that, in the presence of the complexes, the cathodic hydrogen evolution reaction was influenced as evidenced by the shift of the potential to more negative values. The effect depends on the structural nature of the β -diketonato ligands, being more pronounced in presence of the $[\text{Co}(\text{Tmhd})\text{cyclam}](\text{ClO}_4)_2$ complex.

The inhibiting effect of the $[\text{Co}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes was studied on the corrosion of iron in perchloric acid solution. The results of the polarization measurements are presented in Fig. 6. According to the electrochemical results,

the cobalt(III) complexes exhibit anticorrosion properties. Compared with an inhibitor-free solution, these inhibitors decrease the corrosion current. A similar range of inhibitor efficiency was found for the complex with Tmhd > Hfac ligand.

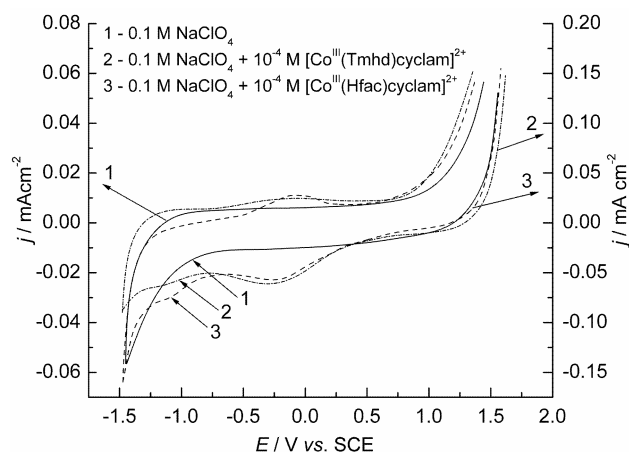


Fig. 5. Cyclic voltammograms at a GC electrode in 0.10 M NaClO_4 without and with 10^{-4} M $[\text{Co}^{\text{III}}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes (sweep rate: 50 mV s^{-1}).

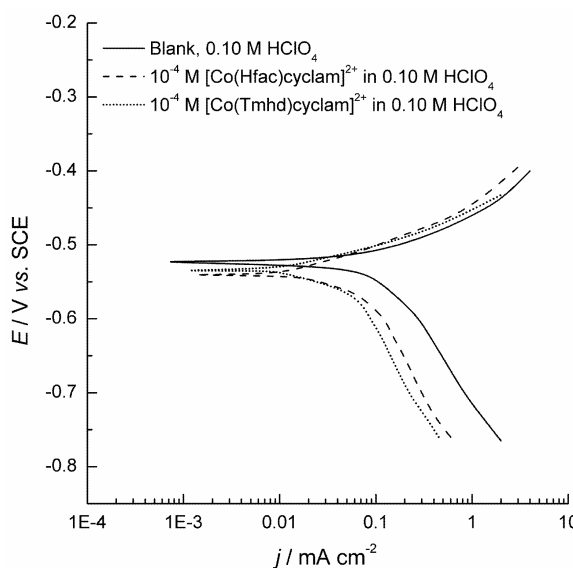


Fig. 6. Polarization curves for iron in 0.10 M HClO_4 and in the presence of 10^{-4} M $[\text{Co}^{\text{III}}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes (sweep rate: 1.0 mV s^{-1}).

IR Spectroscopy data of the $[\text{Co}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes are summarized in Table II. Based on the spectral data, it was observed that R groups on the β -diketone influence the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ band frequencies, due to different resonance and inductive effects along the conjugated double bonds through the Rac^- anion, in the order $\text{Hfac} > \text{Tmhd}$ ligand. The presence of the trifluoromethyl group, due to the electron-

withdrawing effect, decreases the electronic density and consequently shifts CC and CO bands toward higher frequencies. On the contrary, due to the positive inductive effect of the methyl group, the other complex showed strong but opposite effects in its IR spectrum. β -Diketonato protons have an “aromatic” character and the chemical shifts in the NMR spectra are under the direct influence of the R groups. The powerful efficacy of the six fluor atoms of the Hfac ligand moves the chemical shifts strongly downfield.

TABLE II. Selected IR spectral data (cm^{-1}) of the $[\text{Co}(\text{Rac})\text{cyclam}](\text{ClO}_4)_2$ complexes

Complex	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$
$[\text{Co}(\text{Tmhd})\text{cyclam}](\text{ClO}_4)_2$ (3)	1560 _s ^a 1549 _s	1507 _m
$[\text{Co}(\text{Hfac})\text{cyclam}](\text{ClO}_4)_2$ (4)	1627 _m 1576 _s	1530 _w

^a_s: Strong; _m: medium; _w: weak

Some molecular parameters were calculated within the framework of SCF-MO using the Zindo/1 method. The optimized structure for the complex that exhibits the better inhibiting effect on iron corrosion is presented in Fig. 7. The total charge density of the molecules is displayed typically on and around the central metal ion and the delocalized part of the molecule, typically the oxygen atom. Orientation of such a large complex molecules towards the metal surface is important and, therefore, it is an electronic effect.

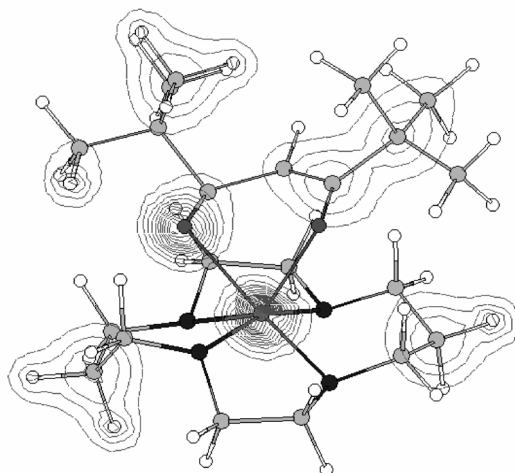


Fig. 7: Zindo/1 optimized structure for the complex $[\text{Co}(\text{Tmhd})\text{cyclam}]^{2+}$; total charge density.

Based on MO calculations, some global reactivity parameters can be established. For the compound with a large dipole moment, a chemical bond with a metal surface may be stronger than that for adsorbed water. If this is the case then the inhibitor might displace the water molecules and adsorb *via* electrostatic bonding. As calculated by the Zindo/1 method, the $[\text{Co}(\text{Tmhd})\text{cyclam}](\text{ClO}_4)_2$ com-

plex has a dipole moment of 12.76 D, as well as high global softness and electrophilicity. This complex exhibits a high inhibition effect. This criterion aids in the understanding of the mechanism of inhibitor function, although it cannot be used as a general principle for such a complex entity because the reactivity of the molecule is defined not only by global indexes but also by the local selectivity of every atom of the molecule when it participates in the corrosion process.²³

CONCLUSIONS

Based on the obtained results, some conclusions and correlations between the structure and electrochemical properties of the examined complexes can be made.

The electrochemical behavior depends on the bidentate dithiocarbamate or β -diketonato ligand. The effects of the complexes manifested themselves on the evolution of hydrogen and the dissolution of iron, with the Rdtc⁻ ligand as 2-Mepipdtc > Timdtc and with the Rac⁻ ligand as Tmhd > Hfac.

The [Co(2-Mepipdtc)cyclam](ClO₄)₂ complex is a weaker catalyst for oxygen reduction than the [Co(Timdtc)cyclam](ClO₄)₂ complex but is more efficient as a corrosion inhibitor. The presence of the methyl group results in the $\nu(\text{CN})$ bond frequencies being shifted to lower energies. The deshielding effect on the >NCS₂ resonances indicates a stronger metal–ligand bond due to the inductive effect of the methyl group. The stronger metal–ligand bond in the complex leads to a higher electron density on the adsorption part of the molecule and, thus, to higher inhibition. Regarding the molecular parameters, a lower ionization potential and energy gap reflects in a stronger chemisorption and perhaps a greater inhibitor efficiency.

In case of the diketonato ligands, the [Co(Tmhd)cyclam](ClO₄)₂ complex influence the hydrogen evolution reaction more, thus exhibiting a higher inhibition effect on the corrosion of iron. As calculated by the Zindo/1 method, its higher dipole moment, as well as high global softness and electrophilicity are in correlation with its inhibitor properties.

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ИЗВОД

КОРЕЛАЦИЈА МОЛЕКУЛСКЕ СТРУКТУРЕ И ЕЛЕКТРОХЕМИЈСКИХ СВОЈСТАВА КОБАЛТ(III) КОМПЛЕКСА СА МЕШОВИТИМ ЛИГАНДИМА

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Четири мешовито-лигандна кобалт(III) комплекса опште формуле [Co(Rdtc)cyclam](ClO₄)₂ и [Co(Rac)cyclam](ClO₄)₂ (cyclam = 1,4,8,11-тетраазациклотетрадекан; Rdtc = тиоморфолин-

-(timdte) или 2-метилпиперидин-(2-meripdte) дитиокарбамат; Рас = 1,1,1,5,5,5-хексафлуоро-2,4-пентанедионато (hfac) или 2,2,6,6-тетраметил-3,5-хептанедионато (tmhd)) испитана су електрохемијски на електродама од стакластог угљеника и гвожђа у раствору перхлората. Добијени резултати указују на то да ови комплекси утичу на издвајање водоника, редукцију кисеоника као и на растварање гвожђа. Електрохемијско понашање зависи од структуре координованог бидентатног дитиокарбамато или β -дикетонато лиганда. Молекулска структура комплексних једињења одређена је на основу спектроскопских анализа и молекулског моделовања. Електрокаталитички и инхибиторски ефекат повезан је са молекулском структуром комплекса.

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