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Electrochemical Engineering Study of Heteroaromatic Molecular Protective-films to Metal-Alloys

Desmond TC Ang [a,*], Peter Junk [b], Glen Deacon [c] and Maria Forsyth [c]

[a] On-Time Engrg Consultant, Singapore, URL:https://www.linkedin.com/t-c-desmond-ang-march6

[b] Nevitt Prof. of Chemistry, College of Sci & Engrg, James Cook's University, Townville, Qld 4811, Australia

[c] Monash University, School of Chemistry, Clayton, VIC 3800, Australia

[*]**Corresponding author:** Desmond TC Ang,

Email: angtc2013@gmail.com or angtc2008@yahoo.com.au

Abstract

The syntheses and characterisation of Rare-Earth-Metals (REMs) heteroaromatic complexes, via the use of green organic esters such as Pyridinecarboxylate (Pyc) or heteroaromatic organic to form stable compounds ie. Lanthanide-Pyridinecarboxylate (Ln-Pyc), has been demonstrated to be one of the preferred compounds to form a good protective-film over metal-alloys. The electrochemical techniques of Linear Polarisation Resistance (LPR) and Cyclic-Potentiodynamic Polarisation (CPP) used in the studies demonstrated strong protective properties to the metal-alloys from the *E* corr-potential and the *I* corr-current. This is because the *I* corr-current was reduced by many folds when coupons were immersed in NaCl (0.01M) as a control bulk-electrolyte containing Ln-Pyc complexes. The data has also confirmed that the Ln-Pyc complexes clearly displayed a mixed-type of protective function. Thus, the overall metal dissolution rate of metallic alloys is mitigated and also indicated a healing mechanistic process involves in building a dense molecular composite-films, when the alloy-coupons were immersed into the solution containing REMs complexes. The characterisation of in-situ treated surfaces via the use of ATR-FTIR, FTIR-microscopy spectrum revealed the overall protective characteristics were discussed in this paper.

Keywords: Rare Earth Metals (REMs), Ligands, Heteroaromatic organics, Pyridine, Coordination Chemistry, Electrochemistry, Corrosion.

1. Introduction

Redox reactions of metal-alloys, such as steel-alloys with its environments, are natural dynamic-processes [1] [2] [3] [4] [5] [6]. This work is studying REMs-complexes produced as stable green REMs-compounds, which are used for studying the ability to protect metallic-alloys. The characterisation of REMs-complexes and crystallography structures have been carried out. In summary, the formation of a general composite protective-film is expressed as:

$$\mathbf{[Ln^{III}(L)_n]_{aq.} + y(OH^-) + x(Fe^{II}/Fe^{III})_{aq} + x(L^-)_{aq.} + H_2O \longrightarrow [(Fe^{II/III})_x\,(Ln^{III})_n](L)_{n+x-y}(OH)_y + Ln(OH)_{3\ (ppt.)}} \qquad \textbf{Eq. 1}$$

Electrochemistry defines redox reactions involving the loss of electrons during metal dissolution and is termed as the anodic reaction as in Eq. 2. The partnering reduction reactions are named as cathodic reactions, as in equations 3 and 4, for examples:

$$\mathbf{Metal_{(solid)} \longrightarrow M^{n+}{}_{(electrolyte\ IONS)} + ne^-{}_{(M\text{-}electrons)}} \qquad \textbf{Eq. 2}$$

$$\mathbf{2H^+ + 2e^- \longrightarrow H_{2(gas)}} \qquad \textbf{Eq. 3}$$

$$\mathbf{O_2 + H_2O + 4e^- \longrightarrow 4\ OH^-} \qquad \textbf{Eq. 4}$$

In order to alter the electrochemical kinetics (rate) of metal dissolution is via modification of environments that become one of fundamental methods in combating metal dissolution as corrosion. There was much of prelim-works by researchers at industries and universities. 1970, organic inhibitors described by G. Trabanelli and co-workers in "Mechanism and Phenomenology of Organic-inhibitors" [7]. Researching of organic compounds becomes an important factor to induce a synergistic impact through formation of a reliable chemical binding, the formation of a high-density polymeric-sheet-style (coverage), which shall be resistant against the immediate environments. The present study shows REM-organic complexes enhances the total synergistic impact, due to formation of lanthanide hydroxides $Ln(OH)_3$ in aqueous, which has an inherently low solubility in aqueous, over a wide range of pH between 5.5 to 13 and temperature conditions [8].

1.1 Materials and preparations

1.1.1 Preparation of lanthanide ligand complexes:

A metathesis for synthesis and characterisation of complexes would be described as follow:

REM-organic complexes were produced at 90 +/-5 °C within green aqueous media, $EtOH/H_2O$. Followed by evaporation for the isolation of a single crystal.

Reagents and chemicals:

Ln_2O_3 (99.99 %) and organic acid (99 %) obtained from Sigma-Aldrich. Alkaline hydroxide (0.5M) solutions were prepared from sodium hydroxide or potassium hydroxide pellets and HCl, HNO_3 and H_2SO_4 were of AR grade. NaCl, Na_2H_2-EDTA laboratory grade reagent, were used as received without further purification.

Lanthanide trivalent ion (Ln^{III}) solutions prepared from lanthanide oxides. Concentrations of lanthanide trivalent ion solutions are accurately determined by analysis using the titration with standardised 0.0100 M Na_2H_2-EDTA. Deionised water is always used in all preparation.

1.1.2 Preparation of ligands' salts:

The Na(L) or K(L) prepared by reaction of Ligand (L-H) solution with NaOH or KOH (0.25 M) solution by monitoring the changes of pH to 8.5

Ligand-H + MOH $\longrightarrow$ M(L) + H_2O (where M = K or Na) A general formula of lanthanide-organic complexes is expressed as $[Ln(L)_x(H_2O)_y.\ mH_2O]$.

Where:

Ln = REMs or mixture of rare-earth elements

L = Picolinate (Pic); isonicotinate (Isn) and Citrazinate (Czn) etc.

1.1.3 Preparation of protective REMs-ligand solutions and complexes:

To D.I. water (pH range of 5.6-5.9), slowly stir an adequate amount of lanthanide-ligand complex while maintained temperature at 45 +/- 5 °C for 3 hr. Removal of undissolved particles after solution is cooled to room temperature, add in NaCl 0.01M (10 mM) to inhibitor solutions for testing.

Pyridine is a heterocyclic aromatic compound which is different to aliphatic-N organic compounds due to the N atom being part of the aromatic ring. The N atom is unique in pyridine in terms of the Lewis basicity (electron donor capability). The N atom is inherently rich in electron density with strong Lewis basicity of pyridine. Some example of Ligands' molecular structures under my studies as below

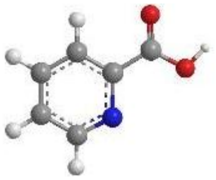


Figure 1-a: 2-Pyridinecarboxlic acid or picolinic acid (Pic-H) (mp = 136 °C)

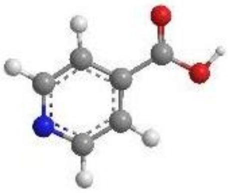


Figure 1-b: 4-Pyridinecarboxlic acid or Isonicotinic acid (Isn-H) (mp = 319 oC)

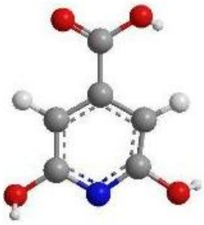


Figure 1-c: 2,6-dihydroxyisonicotinic acid or Citrazinic acid (Czn-H) (mp > 300 oC)

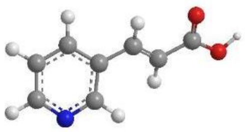


Figure 1-d: 3-(3-pyridyl)acrylic acid (3-Pya-H) mp. 232 oC

The metathesis of sodium Pyc with hydrated LnX_3 salts (X = Cl or NO_3) in water at pH 5.0 resulted in the precipitation of complexes, which were off-white for lanthanum, yellow for cerium and pale green for praseodymium. A general formula of these complexes is presented as $[Ln(Pyc)_3]$**.** mH_2O [Ln = La and Ce]; For an example of $La(Isn)_3(H_2O)_2$ molecular structure as seen in Figure 2.

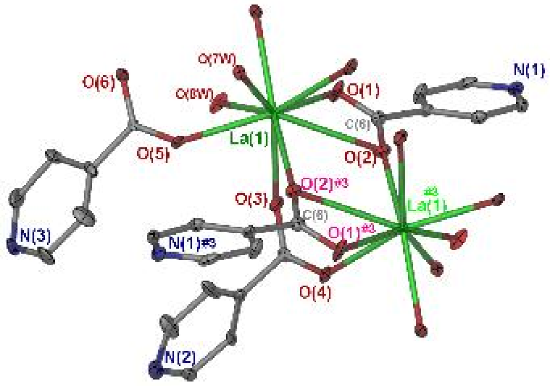


Figure 2: Example of the metallic center atoms (La) and (Pyc) molecular orientation showing how the chelating-bonds are presented in $[La(Isn)_3(H_2O)_2]$ with the heteroaromatic complexes series.

1.1.4 Preparation of steel-alloy coupons:

Specimens are prepared from steel-alloy sheet: nominal composition are C, 0.04 %; Mn, 0.24 %; P, 0.007 %; S, 0.009 % and Fe, balance %. (Australia).

a) Immersion test samples cut size: 25 x 25 x 1 mm for ASTM G31-72 [10].

b) Surface analytical samples size: 10 x 10 x 1 mm for ATR-FTIR, Raman spectroscopy and FTIR-imaging.

c) Electrochemical studies coupons size: 20 x 20 x 1 mm for ASTM G59-91 (LPR); ASTM G61-86 (CPP) [11] [12].

2. Results and discussion of studies

2.1 Overviews of protective-films properties:

To capture kinetic (rate) information, electrochemistry is commonly used as a preferred approach to bring an understanding of metal dissolving mechanistic rate.

The metal-alloy dissolution rate is determined at aqueous environments, in the presence of REMs-complexes in bulk NaCl 100 mM (0.1 M) solution for immersion studies and at 10 mM (0.01 M) for electrochemical measurements of *LPR and CPP (Rp)* respectively.

2.2 Protective-films and in-situ surface characterisation

Lanthanide (REMs) Organic complexes syntheses via a green pathway for preliminary screening to identify preferred potential protective inhibitors. (1) Immersion test [ASTM G31-72] and (2) *LPR* as method [ASTM G59-91].

Immersion test of mass-loss results of ASTM G31-72 summarised in Table 1 and electrochemical data of ASTM G59-91 were recorded in Table 2, which is the measurement of *LPR (Rp)* Ohm.

Table 1: Lab-Immersion test results *(ASTM G31-72),* after seven days within the solutions of different complexes; Against control @ NaCl 0.10 M (100 mM) bulk solution.

($Ln^{(III)}$organic complexes) NaCl	**Dissolution rate (7d) (µg / m^2-s)**	**Relative protective efficacy (%) *****
0.10 M (100 mM)	**33.6 (+/10 %)**	**control bulk soln.**
Isn (isonicotinate) Ln (Ln =La; Ce; Pr)	**15; 18; 18**	**46; 55; 56**
Pic (picolinate) Ln (Ln =La; Ce; Pr)	**27; 15; 18**	**19; 46; 45**

*** Protective efficacy % = [($rate_{(control)}$ – $rate_{(sample)}$) / $rate_{(control)}$] x 100 %

2.3 Electrochemical applications of *LPR* and *CPP*

2.3.1 Linear-Polarisation Resistance *(LPR)* (ASTM G59-91)

Table 2: ASTM G59-91 Linear Polarisation Resistance *(LPR)* R_p(ohm) measured and tabulated

Ln^{III} (Pyc) Lanthanide Pyridinecarboxylate complexes	***Rp* (K ohm) / $E_{oc}(V)_{(SCE)}$**	**Protective efficacy % *****

NaCl 0.01 M (10mM)	**1.9 / - 0.55 V**	**0**
Isn (isonicotinate)		
La (0.41 mM)	**4.8 / -0.39V**	**60.4**
Ce (0.40 mM)	**5.5 / -0.37V**	**56.4**
Pic (picolinate)		
Ce (0.39 mM)	**3.2 / -0.31V**	**40.6**
Czn (citrazinate)		
La (0.04 mM)	**9.66 / -0.47V**	**80.3**
Ce (0.04 mM)	**12.4 / -0.43V**	**84.7**
Pr (0.04 mM)	**12.8 / -0.48V**	**85.2**
3-Pya [(3-pyridyl)3-acrylate]		
La (1.66 mM)		
Ce (1.66 mM)	**7.3 / -0.35V**	**73.9**
Pr (1.66 mM)	**6.5 / -0.38V**	**70.8**
	7.1 / -0.36V	**73,2**

(***)Protective Efficacy %= $[(R_{p\ (\text{sample})} - R_{p(\text{control})}) / R_{p(\text{sample})}]$ x 100%

Review (1): The results from both immersion-tests and *LPR* electrochemical data indicated that lanthanide Pyc complexes perform well in terms of the protective efficacy for metallic-alloys. This showed a stable poly-heteroaromatic-composite protective film, which consists of carboxylate and nitrogen atoms, would play a synergistic role in mitigating the dissolution of metallic-alloys.

2.3.2 *CPP* data analysis of additives containing Ce(Isn)

The *CPP* scan-plots of Ce (Isn) solution at two different concentrations, Figure 5, indicated that both the anodic and the cathodic current density arms are suppressed. It appears that this Ce(Isn) complex is a truly mixed-type of protective function, mitigating the dissolution-rate of steel-alloy as indicated. At a much lower range of i_{corr} current density (µA/cm^2).

An added promising value of *CPP* data as seen in Figure 6, has clearly shown an outstanding performance of Ce(Czn) on the reduction of metallic dissolution rate within comparison of Ce(Isn)@ 0.92mM and Ce(Czn)@ 0.04 mM charts.

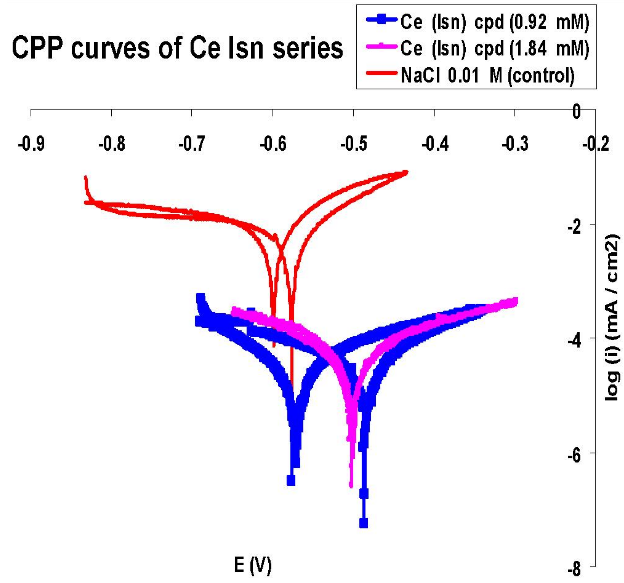


Figure 5: CPP scan-plots of Ce (Isn) complexes Ce (Isn) (0.92 mM) in blue, Ce (Isn) (1.84 mM) in pink @NaCl (0.01 M) Control solution (zero inhibitor) in red

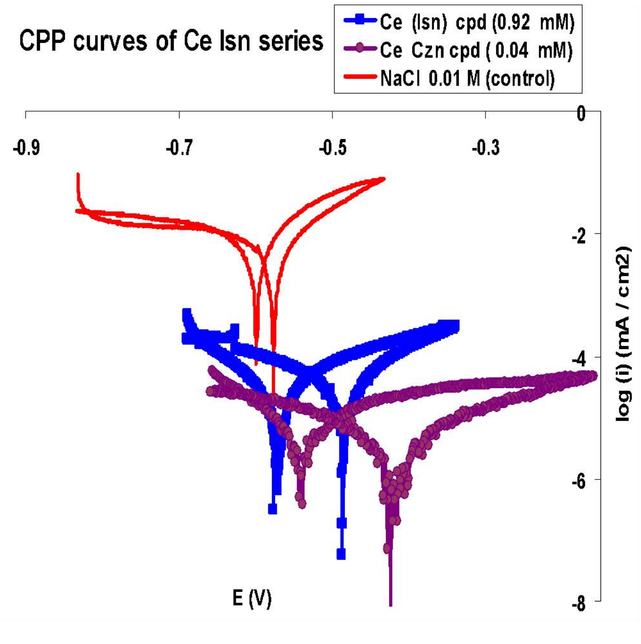


Figure 6: CPP data curves of Ce Isn and Ce Czn complexes Ce (Isn) (0.92 mM) in blue, Ce (Czn) (0.04 mM) in purple @ NaCl 0.01 M Control bulk-solution in red.

Table 3: *CPP* Electrochemical data of Ce(Isn) series extracted after the *CPP* scanning tests. @NaCl 10 mM (0.01 M). All tests were conducted with conformance to the ASTM G3-89 procedure.

Complexes	conc mM	$E_{oc\ (V)}$	$E_{corr\ (V)}$	log $i_{corr\ (mA/cm2)}$	$i_{corr\ (\mu A/cm2)}$
NaCl control	10	-0.65	-0.59	-2.13	7.41
CeCl$_3$ hydrated	0.4	-0.68	-0.67	-3.52	0.302
Ce (Czn)	**0.04**	**-0.52**	**-0.54**	**-4.59**	**0.026**
Ce (Isn)	0.92	-0.54	-0.58	-4.25	0.056
Ce (Isn)	1.84	-0.51	-0.51	-4.08	0.083
Ce (3-Pya)	0.51	-0.21	-0.21	-3.29	0.513

Where:

E_{oc} = open circuit after 24 h to achieve equilibrium state

E_{corr} = CPP forward scan corrosion potential

I_{corr} = CPP forward scan current density (mA / cm^2) at E_{corr}.

Review (2): Comparison of *CPP* data of Ce(Isn) and Ce(Czn) studies. Analysis of Electrochemical CPP data on E_{corr}, E_{rp} and i_{corr} has given a promising indication of a protective-film formed in the presence of REMs complexes. Investigation of the electrical scanning data showed evidence of the synergy impact of the REMs complexes, displayed as the synergistic mixed-type anionic and cathodic protective function, and perform well at a relatively low concentration.

2.3.3 In-situ surface characterisation by spectroscopy

2.3.3.1 Lanthanide Isonicotinate Ln(Isn) ATR-FTIR:

The ATR-FTIR spectra comparison table shows the shifted bands of Ce^{III} (Isn) and Fe^{II} (Isn) between the metal-ligand binding region (500 to 1000 cm^{-1}). The strong possibility of bimetallic compounds co-existed on the steel surface have been certified.

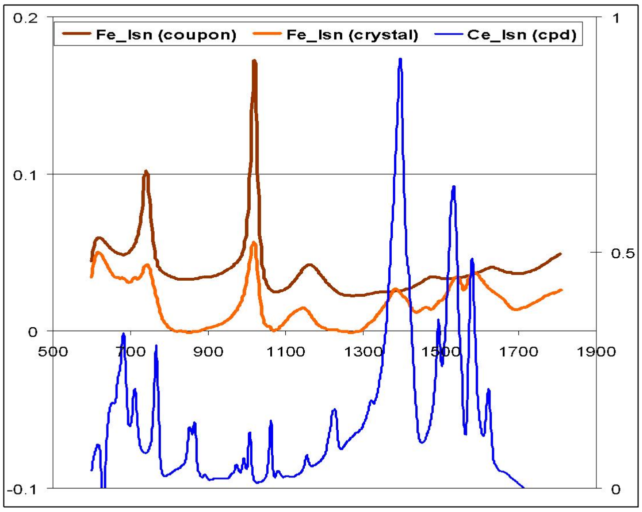


Figure 7: ATR FTIR spectra bands of Fe (Isn) and Ce (Isn) compounds with assignments Table 4; zoom view between the frequencies of 500 to1800 cm^{-1}

Table 4:

Table 4					COO ע
Isn Cplx	Metal-O ע(cm^{-1})				(sym)
Ce(Isn) (cpd)	680	766	1006	1152	1395
Fe(Isn) (crystal)	**618**	**743**	**1018**	**1145**	**1375**
Fe(Isn) (coupon)	**619**	**742**	**1019**	**1161**	**1377**

2.3.3.2 Lanthanide Citrazinate complex Ln(Czn) ATR-FTIR:

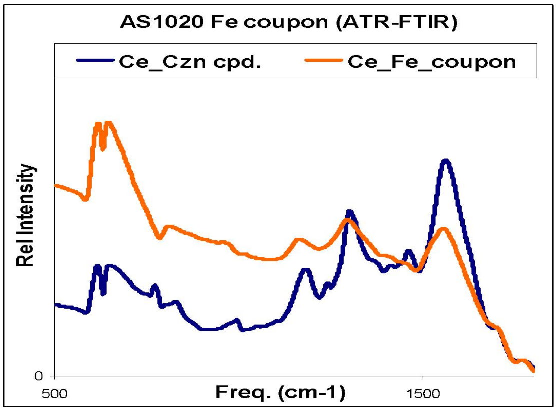


Figure 8: Selected FTIR bands frequencies of Ce (Czn) Blue and treated-steel coupons Orange with assignment Table 5; zoom view between the frequencies of 500 to 1800 cm^{-1}

Table5

Czn Cplx	Metal-O ע(cm^{-1})			C-OH'	C-OH"	COO ע$_{(asym)}$
Ce(Czn)	611	641	983	1172	1296	1555
steel	612	639	962	1150	1282	1545

Interestingly, it was noted that the FTIR spectra had very little changes for the major absorption bands between the one month and the two-hour test coupons. Besides the intensity was ten-fold stronger from the one-month test coupon. Thus, it might have suggested that a reliable molecular protective-film was stable throughout the entire study period of one-month immersion. The formation of low solubility compounds appeared to form a relatively strong and stable film which was resistant to an aqueous solution containing chloride anions.

2.3.4 Modeling of metal-alloy protective film surface analysis and investigation to work with different metallic-alloys.

A light yellow single crystal of [Fe(Isn)$_2$(H$_2$O)$_4$] (see Figure 9) isolated from steel-alloy-coupon under a neutral aqueous solution containing [Ce(Isn)$_3$]**.** A modeling experiment by pre-cleaned steel-alloy coupon immersed in a saturated solution of [Ce(Isn)$_3$] at neutral pH. The objective is to simulate that dissolution of metal-alloys taken place around natural pH conditions [5].

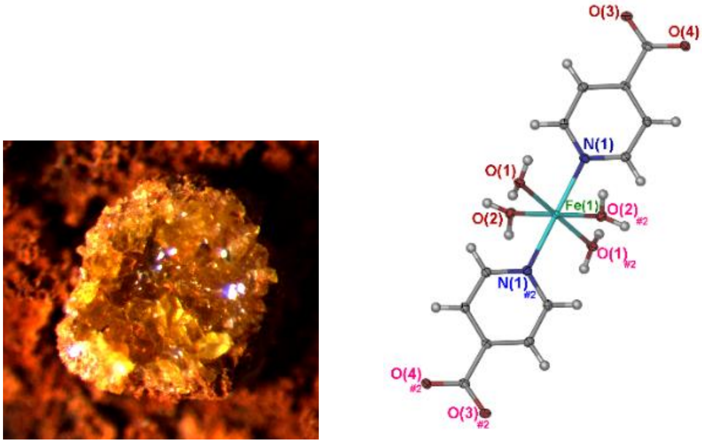
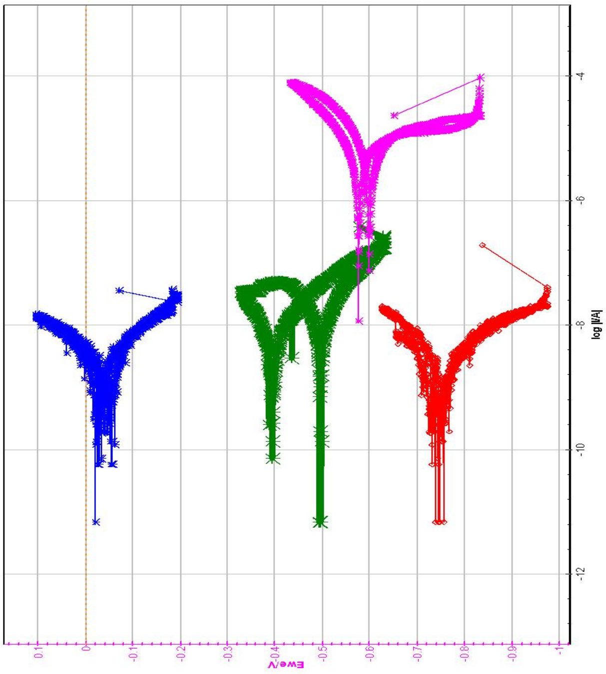


Figure 9: Molecular structure of yellow-crystal **[Fe(Isn)$_2$(H$_2$O)$_4$]$_\infty$** $C_{12}H_{16}Fe_1N_2O_8$ [FW372.12]

Showing that the octahedral Fe center bound by two

trans N-isonicotinate ions, that showed a uniqueness of N atoms of hetro-cyclic aromaticity.

2.3.5 Additional investigations were conducted with an objective is to explore my prelim results of work, for more potential of REMs-ligand complexes. Thus, electrochemical engineering studies has been carried out for future references, such as the use of different REMs organic complexes to test with different metallic-alloys: the example as follows is the summary of the *CCP* data chart of **Blue (copper)** and **Red (Aluminum)** as part of my preliminary study of metallic-alloys.



3. Conclusion

The prelim results derived from the immersion-tests and followed up with *LPR/CPP* electrochemical studies are presented in Table 1 and 2. We are confident that REMs-Pyc complexes perform well in terms of the protective efficacy for metallic-alloy. The Lanthanide complexes have interestingly illustrated that it has formed a strong stability of protective-film under test of environmental condition, and exhibited a symptom of auto-healing effect which could occur in real-life applications.

Metal's dissolution processes are indeed a series of hetero-chemical reactions; they are environmentally dependence. Therefore, to mitigate metallic corrosion issues of metal-dissolution is required, and propose best approach is combining technologies of science and engineering of electrochemistry.

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