Inhibitive effect of Halophosphonic acid on the corrosion of carbon steel in sea water

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---ABSTRACT---

Inhibition of carbon steel corrosion in sea water medium by 2-Chloroethylphosphonicacid (2-CLEPA), Trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSC) and Zn^{2+} ions was investigated by weight loss measurement, potentiodynamic polarization, , Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Energy dispersive X-Ray spectroscopy (EDS). The results indicated that the TSC acts as an optimum in the inhibition efficiency (97%) is observed for a concentration close to 300 ppm. Potentiodynamic polarization studies inferred that this mixture functions as a cathodic inhibitor. Surface characterization techniques (FT-IR, SEM, EDS are also used to ascertain the nature of the protective film. The mechanical aspect of corrosion inhibition is proposed.

Keywords - *2-Chloroethylphosphonicacid (2-CLEPA), Carbon steel, Polarization, FT-IR, SEM, EDS.*

I. INTRODUCTION

Corrosion inhibitors have long been used for daily operation of recirculating cooling water system, industrial acid cleaning, oil well acidification, and descaling due to their economical and efficient properties. [1–3] Organic compounds are recognized as effective inhibitors of the corrosion of many metal and alloys. The efficiency of an organic compound as a corrosion inhibitor is closely associated with the chemical adsorption.[4-8] Most of these organic compounds contain nitrogen, sulphur, oxygen and multiple bonds in the molecules which are adsorbed on the metal surface and the organic compound. [9, 10] Phosphonic acids have ability to control the corrosion of various metals. [11-16] Generally Phosphonic acids are organic compounds containing $R-PO(OH)_2$ or $R-PO(OR)_2$ groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion. Phosphonic acids are extensively used now-a-days due to their complex forming abilities, high stability under harsh conditions, and low toxicity. [17-19] The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents. Compounds with a phosphonic functional group are considered to be the most effective chemical for inhibiting the corrosion process and it is well known that short chain- substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels.

The aim of the present work is to determine the inhibitive effect of 2-Chloroethylphosphonicacid, TSC and Zn^{2+} ions on the corrosion of carbon steel in sea water medium by chemical and electrochemical methods. Surface characterization techniques (FT-IR, SEM, EDS) are also used to ascertain the nature of the protective film.

II. EXPERIMENTAL

2.1. Materials

2-Chloroethylphosphonicacid (2-CLEPA), Zinc sulphate ($ZnSO_4.7H_2O$), Trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSC) and other reagents were analytical grade chemicals. The molecular structures of 2-Chloroethylphosphonicacid and Trisodium 2-hydroxypropane-1,2,3-tricarboxylate are shown in Fig. 1 and 2 respectively. All the solutions were prepared by using double distilled water. An aqueous solution consisting of sea water has been used as the control throughout the studies.
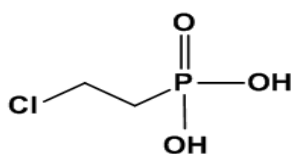
Fig.1. The molecular Structure of 2-Chloroethylphosphonicacid (2-CLEPA)
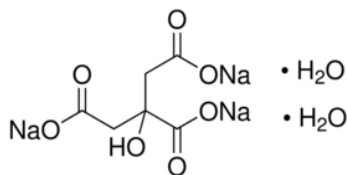

Fig. 2. The molecular structure of Trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSC)

2.2. Preparation of specimens
For all the studies, the specimens taken from a single sheet of carbon steel of the following composition were chosen: C, 0.1-0.2%; P, 0.03-0.08%; Mn, 0.4-0.5% and the rest iron. For gravimetric measurements and surface analytical techniques, the polished specimens of the dimensions, 4 cm x 1.0 cm x 0.1 cm, were used while for other (electro chemical) studies, the dimensions of the specimens were 1.0 cm x 1.0 cm x 0.1 cm Prior to all measurements, the specimens were polished successively using 1/0 to 6/0 emery papers, decreased with trichloroethylene and washed thoroughly with double distilled water and dried.

2.3. Gravimetric studies
Gravimetric experiments are the easiest way to find the corrosion rate (CR) and inhibition efficiency (IE). In all gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 ml control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of one day. Then, the specimens were reweighed after washing and drying. The weights of the specimens before and after immersion were determined by the Mettler electronic balance, AE 240 model with a readability of 0.1 mg. Accuracy in weighing up to 0.0001g and its surface area measurement up to 0.1 cm^2. The corrosion inhibition efficiency was calculated according to the following equation.
Inhibition efficiencies (IE) of the inhibitor were calculated by using the formula,

$$\text{I.E} = 100\,[1 - W_2/W_1]\,\% \tag{1}$$

Where,
W_1= Corrosion rate in the absence of inhibitor
W_2= Corrosion rate in the presence of inhibitor.

2.4. Electrochemical studies
Electrochemical potentiostatic polarization studies were carried out using an electrochemical workstation CHI model 660A (USA) electrochemical analyzer. The carbon steel specimens used as working electrode while platinum and calomel electrodes were used as counter electrode and the reference electrode, respectively. Polarization measurements were carried out at E_{corr} potential at the range of 100 kHz to 10 mHz at amplitude of 10 mV. The polarization parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic tafel slope (β_a) and cathodic Tafel slope (β_c) were computed from the polarization curves. The IEp values were calculated from potentiodynamic polarization measurements using the equation (2).

$$\tag{2}$$

Where, I_{corr} and I'_{corr} are the corrosion current densities in case of the absence and presence of the inhibitor respectively.

2.5. Surface examination studies
The carbon steel specimens were immersed in various test solutions for a period of one day. Then, they were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS).

2.5.1. Fourier transform infrared spectroscopy

The carbon steel specimens were immersed in various test solutions for a period of one day. On completion of the one day, the specimens were taken out and dried. The protective film formed on the metal specimens was scratched and mixed with KBr and pellets were obtained and the FT-IR spectra were recorded using Spectrum RXI Spectrophotometer over a range of 4000 - 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.5.2 Scanning electron microscopy and EDS

The surface morphology of the formed layers on the carbon steel surface after its immersion in control solutions containing sea water in the absence and in the presence of the inhibitor were carried out. After one day, the specimens were taken out, washed with distilled water and dried. The SEM- EDS photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

III. RESULTS AND DISCUSSION

3.1. Gravimetric studies

The gravimetric measurements were carried out to calculate the corrosion rate (CR) and inhibition efficiency (IE) for the carbon steel in an aqueous solution containing sea water in the absence and presence of various inhibitor formulations consists in various amounts of 2-CLEPA, Zn^{2+} ions and TSC are given in Table 1. The inhibition efficiency was represented as a function of TSC concentration in Fig. 3.

Table 1: Inhibition efficiency (IE) and Corrosion rate (CR) by gravimetric studies of carbon steel in the presence of inhibitor

Zn^{2+} (ppm)	2-CLEPA (ppm)	TSC (ppm)	Weight loss (g)	I.E (%)	Corrosion rate (mdd)	Surface Coverage (θ)
Blank	--	--	0.0031	--	28.18	--
20	100	50	0.0005	84	04.54	0.8387
20	100	100	0.0004	87	03.63	0.8709
20	100	150	0.0003	90	02.72	0.9032
20	100	200	0.0002	93	01.81	0.9344
20	100	250	0.0001	95	01.36	0.9516
20	100	300	0.0001	97	00.90	0.9677

The results of the ternary formulations, that for lower concentration of 20 ppm Zn^{2+} and 100 ppm 2-CLEPA with 300 ppm TSC, the maximum inhibition efficiency of only 97% is achieved. A further addition to increasing the TSC concentration increasing order of the inhibition efficiency.
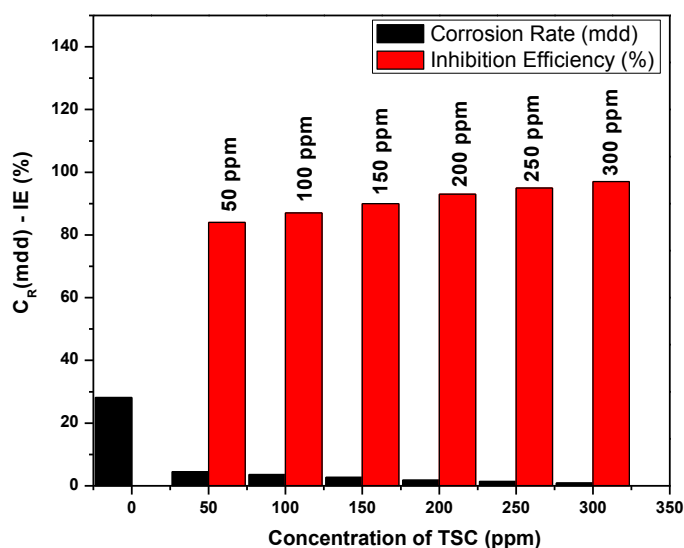

Fig. 3. Inhibition efficiency as a function of concentration of TSC

3.2. Electrochemical measurements
3.2.1 Potentiodynamic polarization studies

The potentiodynamic polarization studies were carried out to determine the kinetics of the cathodic and anodic reactions. Fig.4. Shows the potentiodynamic polarization curves for carbon steel electrodes in control solution in the absence and presence of various inhibitor combinations. Electrochemical kinetic parameters, i.e., the corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic and cathodic tafel slopes (β_a and β_c), obtained from extrapolation of the polarization curves are listed in Table 2. When carbon steel is immersed in sea water medium, the corrosion potential (Ecorr) is -784 mV/dec and the corrosion current is 26.20 µA/cm². When 300 ppm TSC to 100 ppm of 2-CLEPA and 20 ppm Zn^{2+} are added to sea water medium the corrosion potential is found to be -858 mV/dec and corrosion current is 0.70 µA/cm². The corrosion current decreases from 26.20 µA/cm² to 0.70 µA/cm².
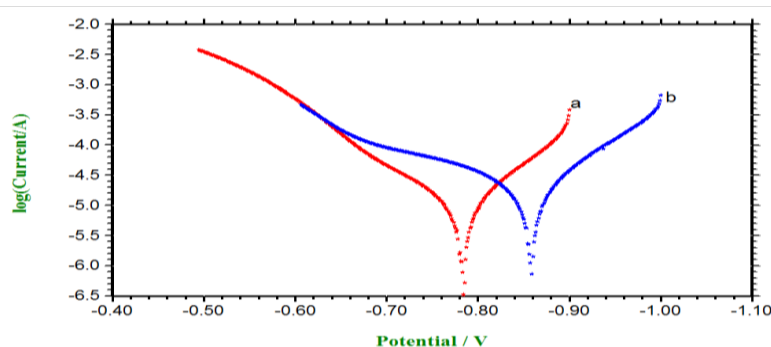
Fig. 4. Potentiodynamic polarization curves of carbon steel in a). Sea Water
b). Sea Water + 20 ppm Zn^{2+} + 100 ppm 2-CLEPA + 300 ppm TSC

This shows that the formulation functions as a cathodic inhibitor controlling both anodic and cathodic processes but more predominantly cathodic process. This suggests, indicate that protective film is formed on the metal surface.

Table 2: Corrosion parameters of carbon steel immersed in the absence and presence of inhibitor obtained from potentiodynamic polarization studies.

Concentration (ppm)	E_{corr} mV/dec)	I_{corr} (µA/ cm²)	b_a (mV/dec)	b_c (mV/dec)	θ	I.E(%)
Blank	-784	26.20	110	78	--	
20 ppm of Zn^{2+}+ 100 ppm of 2- CLEPA + 300 ppm of TSC	-858	0.70	104	86	0.97	97

3.3 surface studies
3.3.1 Fourier transform infrared spectroscopy

The FT-IR spectrum of pure 2-CLEPA is shown in Figure 5(a). The P-O stretching frequency of phosphonic acid group appears at 1159 cm⁻¹. The FT-IR spectrum of pure Trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSC) is shown in figure 5(b). The C=O stretching frequency of carboxyl group appears at 1595 cm⁻¹.
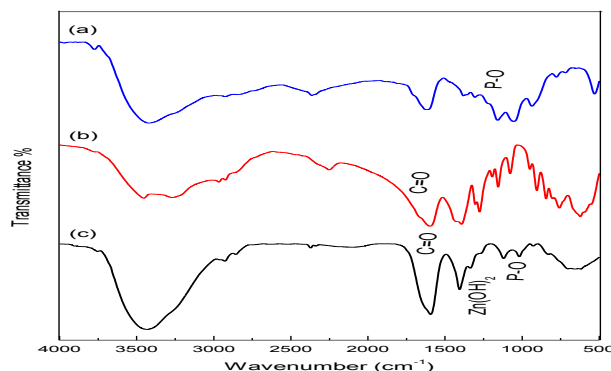

Fig.5. FT-IR Spectra of (a) pure 2-CLEPA (b) pure TSC (c) Surface film

The FT-IR spectrum (KBr pellet) of the film formed on the carbon steel surface after immersion in the water containing 300 ppm of TSC, 20 ppm of Zn^{2+} and 100 ppm of 2-CLEPA in the sea water environment is shown in figure 3(c). The P-O stretching frequency has decreased from 1159cm^{-1} to 1120 cm^{-1}. This shift is caused by the decreased of the electron cloud density from the oxygen atom to Fe^{2+}, it is suggested that oxygen atom of the phosphonic acid is coordinated to Fe^{2+}, resulting in the formation of Fe^{2+}-2-CLEPA complex on the metal surface. In the case of TSC, the C=O stretching frequency has decreased from 1595 cm^{-1} to 1593 cm^{-1}. This indicates that carboxyl group of TSC has coordinated with Fe^{2+} on the anodic sites of the metal surface, resulting in the formation of Fe^{2+} - TSC complex. The peak at 1405 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface. The FT-IR spectra led to conclusion that the protective film consists of Fe^{2+}- TSC complex, Fe^{2+}- 2-CLEPA complex and $Zn(OH)_2$.

3.3.2 Scanning electron microscopy (SEM)

SEM analysis provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extend of corrosion of carbon steel. Fig.6.(a) show the polished metal surface of carbon steel before corrosion Fig.6.(b) show the metal surface immersion of sea water solutions. This shows the roughness of the metal surface by the corrosive environment and there is formation of different forms of corrosion products.
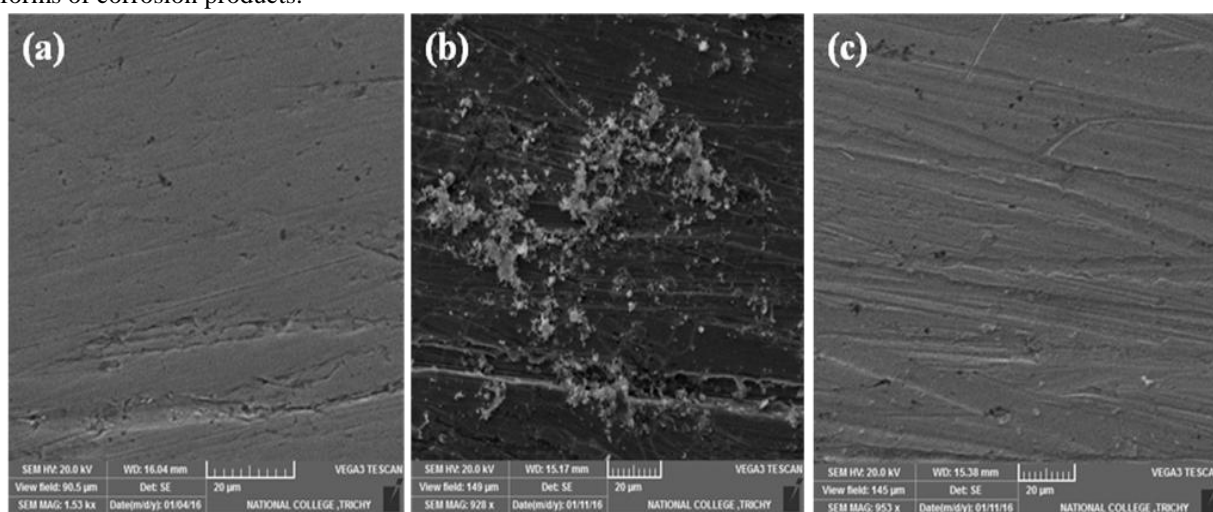

Fig.6. SEM images of carbon steel immersed in a). Polished carbon steel b). Sea Water
        c). Inhibitor solution

Fig.6.(c) show the metal surface immersion of 300 ppm TSC to of 100 ppm 2-CLEPA and 20 ppm Zn^{2+} are added to sea water$^-$ medium gives metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface. Comparative examination of these images, clearly suggest that the surface of carbon steel is smoothened to a very large extent in the presence of the combined inhibitor system. This smoothening might be due to the adsorption of the inhibitor molecules on it and thus the surface is fully covered.

3.3.3 Energy Dispersive X-Ray Spectroscopy (EDS)

The EDS spectra was used to determine the elements present on the surface of carbon steel absence and presence of inhibitors in the uninhibited and inhibited sea water. Fig.7.(a) gives characteristics peaks of the elements (Fe, Carbon and Mn) constituting the polished carbon steel specimen. Fig. 7.(b) portrays the EDS analysis of carbon steel in sea water which indicates only the presence of Fe, Na, Cl and O. This confirms that the passive film contained only Fe_2O_3. The EDS of presence of inhibitor Fig. 7(c) in shows the presence of additional lines due to Fe, C, Na, Cl, Zn and P, O. This may beat tribute to the presence of inhibitor on carbon steel which protects the steel surface from corrosion.
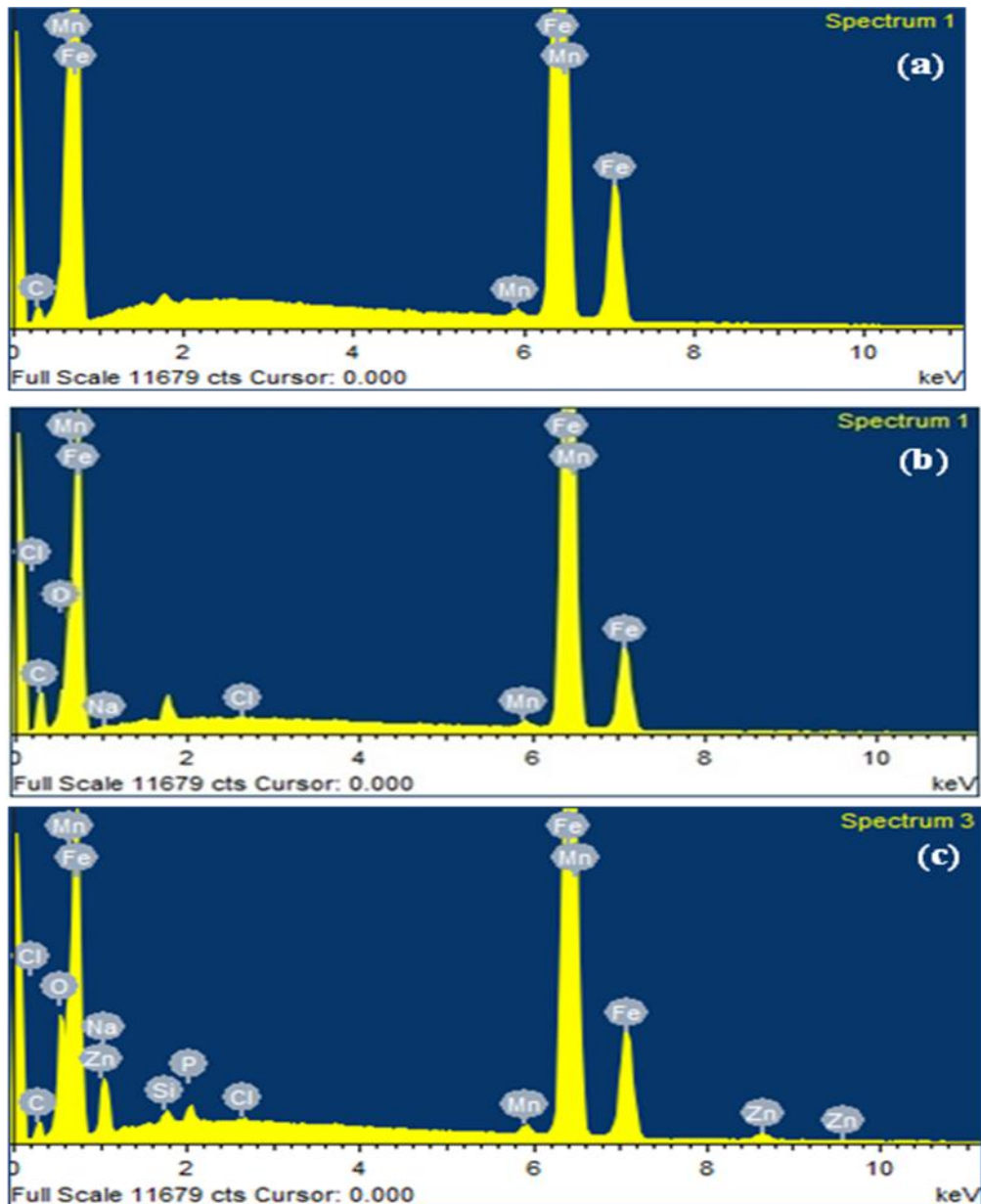
Fig.7. EDS images of carbon steel in a). polished carbon steel b). sea water
c). Inhibitor solution

3.4. Mechanism of protection

In order to explain all the experimental results, the following mechanism of corrosion inhibition can be proposed. Carbon steel undergoes initial corrosion to form Fe^{2+} ions at anodic sites:

(3)

Fe^{2+} further undergoes oxidation in the presence of oxygen available in the aqueous solution:

(4)

And the cathodic reaction is:

(5)

When the environment containing sea water/20ppm Zn^{2+}/100 ppm 2-CLEPA/300 ppm TSC was prepared, a $[Zn^{2+}$-2-CLEPA-TSC] complex was formed in the solution. Besides this complex, the presence of free 2-CLEPA, TSC and Zn^{2+} ions. While the metal was immersed in this environment, the $[Zn^{2+}$-2-CLEPA -TSC] complex diffused from the bulk of the solution onto the surface of the metal and further complexes with

Fe^{2+}/Fe^{3+} ions available due to initial corrosion. Free 2-CLEPA and TSC molecules diffuse from the bulk of the solution to the metal surface and form $[Fe^{2+}/Fe^{3+}$-2-CLEPA -TSC] complexes. These complexes fill the pores of the film formed on the surface and make it productive.

$$(6)$$

Free Zn^{2+} ions diffuse from the bulk of the solution to the metal surface and form $Zn(OH)_2$ at the local cathodic sites.

$$(7)$$

Thus, 2-CLEPA, Zn^{2+}, and TSC play a very important role in the controlling corrosion through the formation of a protective film on the metal surface.

IV. CONCLUSION

All the results showed that the 2-CLEPA has excellent inhibition properties for the corrosion of carbon steel in aqueous medium. The gravimetric measurements showed that the formulation containing 20 ppm Zn^{2+} ions, 100 ppm 2-CLEPA and 300 ppm TSC yield good inhibition efficiency of 97%. The inhibitor formulation acts as a cathodic in nature. Which is further evidenced from FT-IR ,SEM, and EDS. The protective film may consist of [Fe (III)/Fe (II)/Zn (II)- 2-CLEPA -TSC] complex, $Zn(OH)_2$, and hydroxides and oxides of iron.

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