Synthesis and characterization of Trimethoprim metal complexes used as corrosion inhibitors for carbon steel in acid media

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Abstract

Trimethoprim (TM) is an antibiotic used to treat bacterial infections as well as it is a heterocyclic compound, whose structure consists of 1,2,3-trimethoxybenzene and pyrimidine-2,4-diamine, therefore it can be used as a corrosion inhibitor due to easy production and low price on carbon steel in acidic media by adsorption process. Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes of Trimethoprim were synthesized and also used as a corrosion inhibitor. The Trimethoprim drug and its complexes were characterized by different spectroscopic methods: Ultraviolet-visible, Fourier transform infrared, conductivity measurements, thermal analysis (TG) and magnetic susceptibility measurement. Adsorption process can be attributed to changes in concentration of inhibitors with the acidity of a solution as well as the surface of the metal (carbon steel). The results of the experiment have shown the coordination of the Trimethoprim drug with the transition metal ions through nitrogen of pyrimidinyl ring so that square planar geometry was suggested for Mn(II), Ni(II), Cu(II) complexes while the Cr(III), Co(II) complexes have an octahedral geometry and these complexes have electrolyte properties. Corrosion inhibition on carbon steel was studied using weight loss method in one molar hydrochloric acid solution by organic inhibitor Trimethoprim and inorganic inhibitors (complexes) at different concentrations with different periods of time. The measurements have shown that Trimethoprim reduced the corrosion of the carbon steel surface and also the inhibition efficiency of the complexes increased with increasing concentration. The inhibition efficiency followed the order Co > Cu > Cr in one molar acidic solution.

Keywords: *metal complexes of Trimethoprim, weight loss method, corrosion inhibitor.*

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Introduction

Drugs, polymers and plant extracts used as corrosion inhibitors form protective layers on carbon steel surfaces through adsorption process. Trimethoprim is an antibiotic used in the treatment of bladder infections and travelers' diarrhea and middle ear infections. Also, this pharmaceutical product is considered a highly effective system to inhibit the corrosion processes of steel in different media due to the presence of heteroatoms such as N and O,

that have high adsorption affinity. The adsorption of Trimethoprim compounds on the carbon steel surface is achieved by the interaction between lone electron pairs of heteroatoms and d-orbitals of the metal atoms [1–11]. The use of inorganic inhibitors due to the decomposing of organic compounds with temperature and time [12] for this reason the prepared complexes of TM used as inhibitors [13, 14]. Silver complexes of trimethoprim show stronger antibacterial activity compared to free drugs, these complexes characterized by spectroscopic and elemental analysis, the ligand coordinate through nitrogen of pyrimidine ring [15]. Cu, Zn, Fe, Ti complexes of trimethoprim (TM) characterized by ^{13}C NMR, elemental analysis, electronic spectra and showed good antibacterial activity, the Ti-TM and Cu-TM showed excellent anticancer activity [16]. Cu^{2+}, Zn^{2+}, Pt^{2+}, Ru^{3+} and Fe^{3+} complexes of trimethoprim were prepared and characterized by spectroscopic and elemental analysis, morphology of metal complexes investigated by scanning electron microscopy. The biological activity of the trimethoprim complexes determined by binding to calf-thymus DNA (CT DNA) with UV spectroscopy and cyclic voltmeter, antimicrobial activity of these complexes and antifungal activity have been evaluated and compared with trimethoprim drug [17]. Inclusion complexes of trimethoprim with cyclodextrins in aqueous solution were prepared by several methods and characterized by many techniques and the antimicrobial activity of trimethoprim and the inclusion complexes were measured, the solubility of the drug increased by methyl-β-cyclodextrin and gave stable inclusion complexes [18]. Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and La^{3+} complexes of trimethoprim derivative were prepared, determined by different physical and chemical techniques, the geometry of these complexes were proposed and the derivative act as a bidentate ligand [19]. Trimethoprim used as an inhibitor to prevent the corrosion of carbon steel in acidic environments. This study was done by weight loss and electrochemical measurements, at temperatures range 25–55°C. The surface morphology of carbon steel before and after corrosion in 1.0 M HCl in the presence and absence of trimethoprim was measured by scanning electron microscopy. The inhibition efficiency, increased with inhibitor concentration increasing and decreased with increasing temperature [20]. Trimethoprim derivative synthesized and characterized by spectroscopic techniques, the corrosion inhibition behavior of this compound was studied by electrochemical measurements and gave good protection for the surface of the mild steel in aqueous HCl. The quantum computations were determined for explanations the adsorption mode, the theoretical calculation conformed to the experimental results [21].

The aim of this work is to prepare Cr (III), Mn (II), Co (II), Ni (II) and Cu (II) complexes with Trimethoprim drug and characterize the structure of these complexes by spectroscopy and elemental analysis, then these complexes was used as inhibitors for carbon steel in acidic environment. The inhibition efficiency of this drug with their complexes was calculated according to the weight loss.

Experimental

Instrumentation

Infrared spectra of (TM) complexes were measured by ALPHA FTIR spectrophotometer. The UV-Visible spectra of the complexes were measured using a Shimadzu UV-Vis 160A spectrophotometer. Thermal analyses (TG-DTG) were gained on a LINSEIS (STA PT-1000). Johnson Mattey's magnetic susceptibility balance can be used for paramagnetic and diamagnetic materials. Molar conductivity measurements were carried by Corning conductivity meter 220.

Synthesis of drug complexes

To (2 mole, 0.58 g) of the trimethoprim drug in distilled water (10 ml) slightly heat to dissolve completely a solution of metal ions (1 mole: 0.16 g $CoCl_2 \cdot 2H_2O$, 0.26 g $NiSO_4 \cdot 6H_2O$, 0.25 g $CuSO_4 \cdot 5H_2O$, 0.17 g $MnSO_4 \cdot H_2O$, 0.27 g $CrCl_3 \cdot 6H_2O$) in distilled water (10 ml) was mixed, then refluxed for 5 hours, filtered the solution and evaporate the solvent to give a colored precipitate then wash with distilled water and dried in oven at 50°C.

Corrosion part

The purity of carbon steel alloy was 98.8%. 1 M HCl was prepared by diluting the analytical grade, 37% HCl in distilled water. The metal complexes of CrTM, CoTM and CuTM were being prepared according to the procedure above.

Inhibitor solutions with different concentrations from 100 to 500 ppm were prepared by dissolving amount of the prepare TM and its metal complexes in 50 ml of 1 M hydrochloric acid and the blank solution was prepared as 50 ml of 1 M HCl without inhibitor. Carbon steel specimens are cleaned by different grade emery papers and degreased with acetone. An analytical balance was used to measure the initial weight of each specimen and then the specimens were immersed in 1 M HCl solution with different concentrations of the inhibitor and without inhibitor in a different time at room temperature. Finally the specimens were washed and weighed.

Result and discussion

Infrared spectra of complexes

The drug has two donor nitrogen of pyrimidinyl ring appear at (3465.61 cm^{-1}, 3315.01 cm^{-1}) for $\upsilon_{as}NH_2$ and υ_sNH_2, respectively, these two bands shifted significantly in the spectra of complexes and appear in the region (3402.0–3312.09 cm^{-1}) assigned to coordinate with metal ions.

Bands at (2930.24, 2830.61, 1459.31, 1329.99 cm^{-1}) for $\upsilon_{as}CH_3$, υ_sCH_3, $\delta_{as}CH_3$ and δ_sCH_3, respectively. Bands at 1630.65 cm^{-1}, 1589.88 cm^{-1} can be assigned to C=N, C=C stretching frequencies [22, 23], see Table 1, Figures 1–2.

Ultraviolet-Visible spectroscopy

The drug show band at 295 nm due to $n \rightarrow \pi^*$ transition while the spectra of complexes showed bands at region (227–382) nm which are characteristic for charge transition and ligand field transition. The CrTM complex showed bands at 21739 cm^{-1}, ^4A_2g (F)$\rightarrow$$^4T_2g$ (F) and ligand field transitions. CoTM complex has bands at 17391 cm^{-1}, 16000 cm^{-1}, 15243 cm^{-1} for ^4T_1g (F)$\rightarrow$$^4T_1g$ (P), ^4T_1g (F)$\rightarrow$$^4A_2g$ (F), ^4T_1g(F)$\rightarrow$$^4T_2g$ (F) transitions, respectively, so the geometry of Co(II) and Cr(III) expected octahedral. NiTM complex has a characteristic band at 23809 cm^{-1} for $^1A_1g \rightarrow {}^1A_2g$ transition. CuTM complex showed bands at 15847.86 cm^{-1} and 15600.62 cm^{-1} for $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2Eg$ transitions so that square planar geometry suggested for Cu^{2+} and Ni^{2+} complexes, see Table 1 [6, 23–24].

Table 1. Some characteristic of IR and UV-Vis. Bands of TM and its complexes.

Compound	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	d-d transition	$\upsilon_{as}NH_2$	υ_sNH_2	υ C=N	υ C=C	υ M–N
TM	295	–	3465.61	3315.01	1630.56	1589.88	–
CrTM	382, 358	460	3402.0	3314.0	1635.55	1585.0	501
Mn TM	280, 294	416	3404.01	3315.0	1631.45	1593.02	456
CoTM	227, 271	575, 625, 656	3410.45	3310.0	1635.55	1595.06	450
NiTM	362	420	3430.11	3312.09	1633.11	1595.00	460
CuTM	238, 306, 318	631, 641	3464.06	3316.18	1629.82	1589.16	490

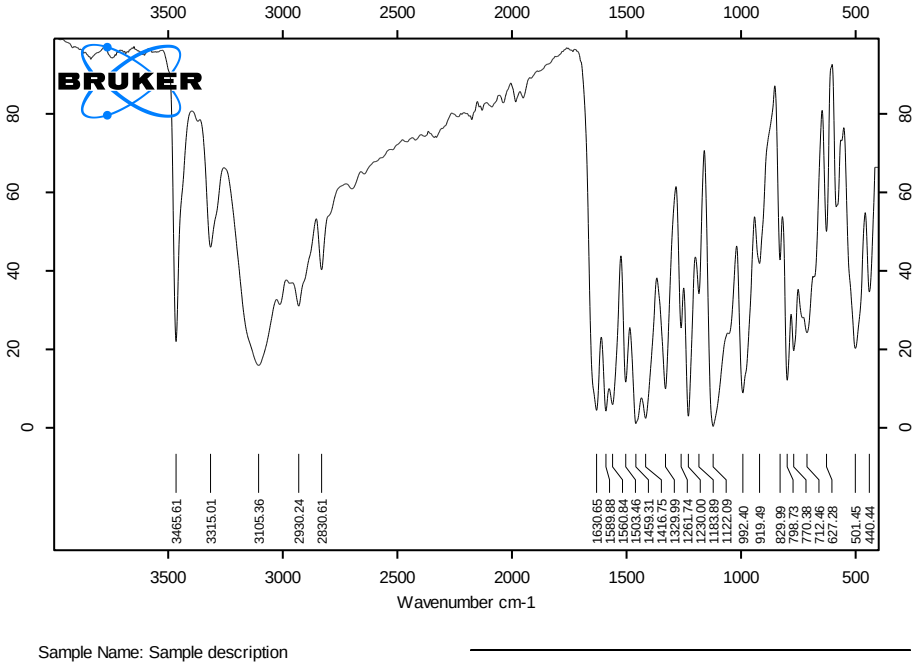


Figure 1. IR spectrum of TM.

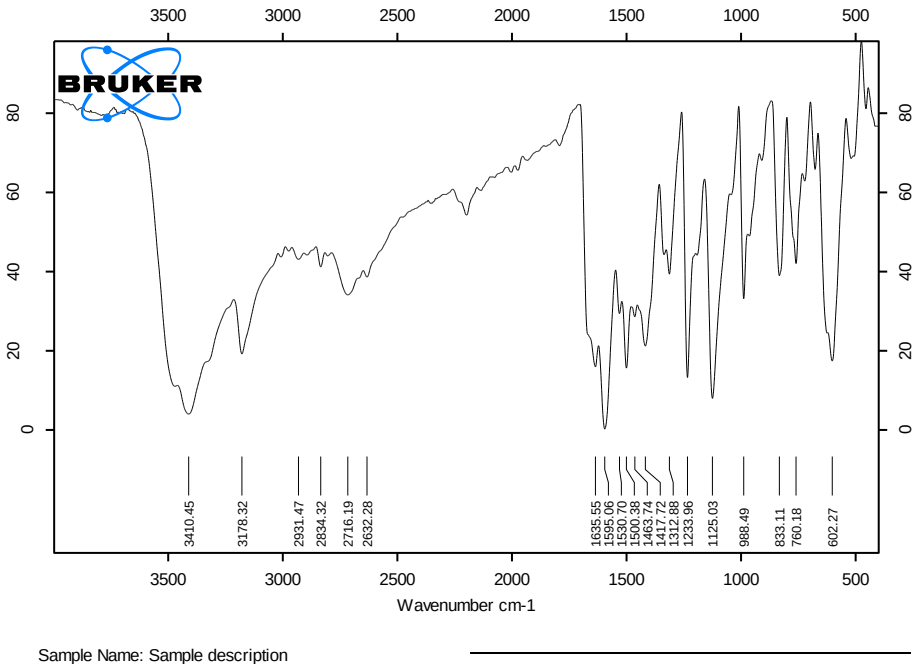


Figure 2. IR spectrum of CoTM.

Table 2. Some physical analysis of TM complexes

Complex	Molecular formal	Color	$\mu_{eff.}$	Conductivity, DMF solvent (µs)
TM	$C_{14}H_{18}N_4O_3$	White	–	–
CrTM	$[CrL_2(H_2O)_2]Cl_3$	Dark green	3.8	210
MnTM	$[MnL_2]SO_4$	Light brown	5.3	70
CoTM	$[CoL_2(H_2O)_2]Cl_2$	Dark pink	4.6	135
NiTM	$[NiL_2]SO_4$	Green	0	66
CuTM	$[CuL_2]SO_4$	Light green	1.9	89

Thermal analysis of metal complexes

Table 3. Thermo analysis of some TM complexes.

Complex	Temperature rang, °C	Weight loss, found (calc.)	Elimination part
$[CrL_2(H_2O)_2]Cl_3$	66–130 330–570	19.12 (18.82) 68.89 (69.27)	$-2H_2O$, –3Cl $-C_{18}H_{22}O_6$ $-4H_2$ $-C_{10}H_6N_4$

$[MnL_2]SO_4$	130–320 390–560	56.00 (54.97) 25.11 (28.89)	$-C_{18}H_{22}O_6$, $-SO_3$ $-C_{10}H_{14}N_4O$
$[CoL_2(H_2O)_2]Cl_2$	55–140 230–500	15.32 (14.68) 74.02 (75.83)	$-2H_2O$, $-2Cl$ $-C_{18}H_{30}O_6$ $-C_{10}H_6N_6$
$[NiL_2]SO_4$	210–288 330–490	45.89 (46.60) 38.10 (39.90)	$-C_{18}H_{22}O_6$, $-C_{10}H_{14}N_4O$, $-SO_3$
$[CuL_2]SO_4$	279–340 380–500	44.89(46.28) 38.00(39.62)	$-C_{18}H_{22}O_6$ $-SO_3$, $-C_{10}H_{14}N_4O$

The thermo-gravimetric technique help to investigate the structure of complexes, $[MnC_{28}H_{36}N_8O_{10}S]$ complex decomposes between 130–320°C to form $[MnC_{10}H_{14}N_8O]$ due to to the elimination part ($C_{18}H_{22}O_6$, SO_3) and the second loss is ($C_{10}H_{14}N_4O$) between 390–560°C to residue $[MnN_4]$. $[NiC_{28}H_{36}N_8O_{10}S]$ complex is assigned to the elimination of ($C_{18}H_{22}O_6$), the other loss of $[NiC_{10}H_{14}N_8O_4S]$ between 330–490°C to remain $[NiN_4]$. The first loss of $[CuC_{28}H_{36}N_8O_{10}S]$ gave $[CuC_{10}H_{14}N_8O_4S]$ at 279–340°C, the other loss at 380–500°C for elimination (SO_3, $C_{10}H_{14}N_4O$) and remain $[CuN_4]$. CrTM and CoTM complexes shows the loss in weight corresponding to water molecules and the remain was $[CrN_4]$ and $[CoN_2]$, respectively, shown Table 3.

Weight loss measurements

The corrosion rate (*CR*) has been estimated from this equation, $CR=(m_1-m_2)/S\cdot t$, (m_1) and (m_2) are masses of the specimen before and after corrosion respectively, *S* area of the specimen, *t* corrosion time. The alloy will be removed and cleaned after each immersion time, then dry and reweight to obtain weight loss. Inhibition efficiency (*PE*, %) was obtained by using the following equation:

$$PE,\ \%=(1-CR/CR^0)\cdot 100$$

CR and CR^0 are the corrosion rate ($mg/cm^2/h$) of carbon steel specimen with and without inhibitors, respectively. ($1-CR/CR^0$) was used to determine the degree of surface coverage (θ). Results showed the inhibitor efficiency (*PE*, %) increased when the concentration of inhibitor increased, the (*PE*, %), (*CR*) and (θ) for CrTM, CoTM and CuTM complexes at different concentrations and different periods of time.

From the data of the experiment the Cr(III), Co(II) and Cu(II) complexes inhibit the corrosion of carbon steel alloy at all concentrations was used in our work. The inhibitor efficiency (*PE*, %) for these complexes, drug increases with increase their concentration, as shown in Figure 3 in 1 M HCl solution.

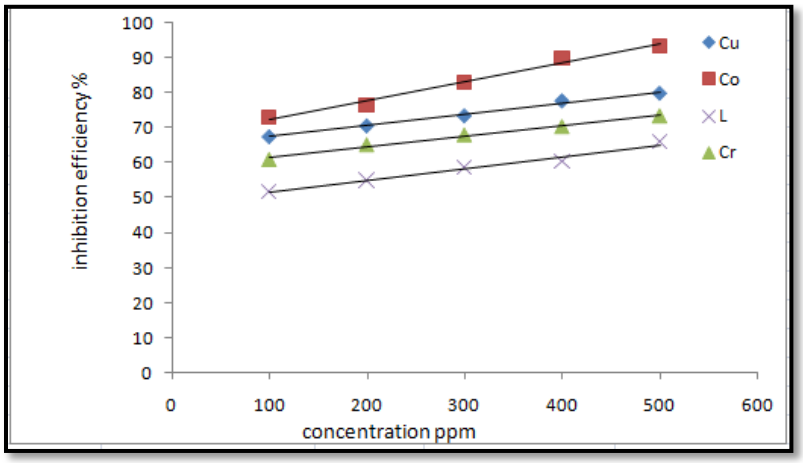
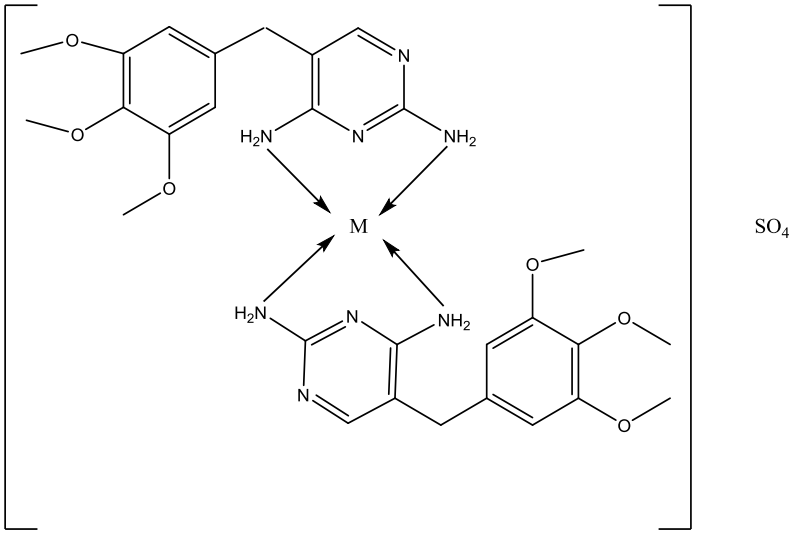


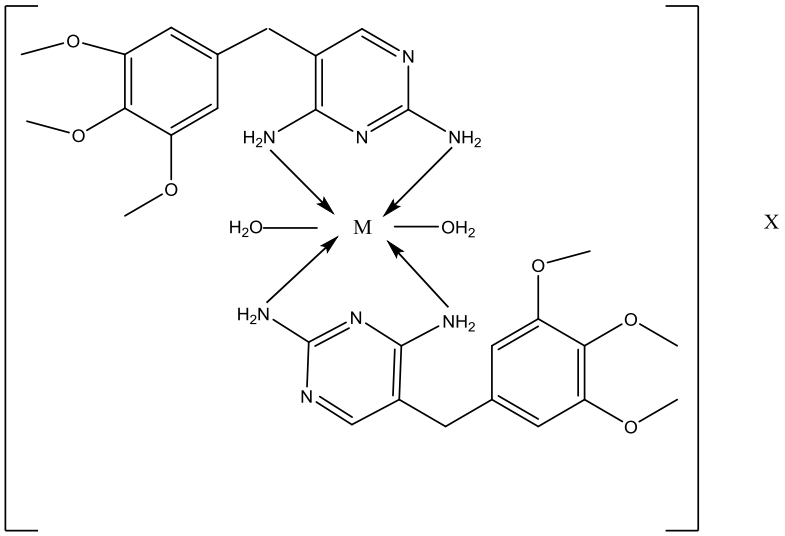
Figure 3. The % *PE* against concentration of metal complexes and TM on carbon steel at 3 hours.

From the above results the geometry of complexes was suggested octahedral conformation for Co(II) with Cr(III) and square planar conformation for Mn(II), Ni(II) and Cu(II), shown in Figures 4 and 5.



M:Ni(II),Cu(II) Mn(II)

Figure 4. Square planar geometry for Mn(II), Ni(II) and Cu(II) complexes.



M:Cr(III) ,X_3=Cl_3
M:Co(II),X_2=Cl_2

Figure 5. Octahedral geometry for Co(II) with Cr(III) complexes.

Conclusion

Complexes of TM were synthesized and characterized. The molar conductivity of these complexes has electrolyte nature. The Ni(II) complex has diamagnetic properties. Octahedral conformation has been suggested for Co(II) with Cr(III) complexes and square planar conformation for Mn(II), Ni(II) and Cu(II) complexes. The inhibition efficiency increases with increase in the concentration of CoTM>CuTM>CrTM complexes.

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