Chemical, electrochemical and surface studies of new metal–organic frameworks (MOF) as corrosion inhibitors for carbon steel in sulfuric acid environment

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The effects of \([\text{Co}_2(\text{SCN})_4(\text{hmt})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]\ (\text{SC}1)\) and \([\text{Co}(\text{CN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}) \cdot (\text{qox})]\) (\text{SCP}2)\) MOF as corrosion inhibitors on \(\text{C-steel}\) in 0.5 M sulfuric acid solutions are illustrated utilizing mass reduction (MR), electrochemical (potentiodynamic polarization (PP), and AC electrochemical impedance (EIS)). The experiments revealed that as the dose of these compounds rose, the inhibition efficacy (IE percent) of \(\text{C-steel}\) corrosion improved, reaching 80.7–93.1% at dose 25 × 10⁻⁶ M for \text{SC}1 and \text{SCP}2, respectively. IE percent, on the other hand, dropped as the temperature range grew. \text{SC}1 was adsorbed physically and chemically (mixed adsorption) but \text{SCP}2 was adsorbed physically on the surface of \(\text{C-steel}\) and conformed to the Langmuir adsorption isotherm equation. The PP studies revealed that these compounds act as mixed kind inhibitors. To establish the morphology of the inhibited \(\text{C-steel}\) surface, scanning electron microscopy (SEM), energy transmitted X-ray (EDX), and atomic force microscopy (AFM) studies were used. All tested experiments were in good agreement.

Because the use of toxic chemicals as inhibitors has been prohibited due to environmental concerns, there is a strong interest in replacing dangerous inhibitors with non-hazardous alternatives1–4. Sulfuric acid is primarily used in the manufacture of fertilizers. It is commonly used in the production of chemicals, medicines and used as pickling agent for metals to remove scales. Corrosion inhibitors have been widely researched in various sectors to reduce the dissolving rate of metal in contact with corrosive environments5–11. The capacity of corrosion inhibitors to absorb on metal surfaces was shown to be associated with their high efficiency12. Adsorption will also be based on the predicted interaction of the inhibitor’s-orbitals with the surface atoms’ d-orbitals. This interaction increases adsorption on the \(\text{C-steel}\) surface, resulting in film-protective corrosion13. The authors concentrated their efforts on utilizing organic compounds as inhibitors that can be obtained, are environmentally friendly, inexpensive, and have renewable sources of obtaining them, and contain heteroatoms such as O, N, S, and multiple bonds in their molecular structure, giving them a strong affinity to inhibit metal corrosion in acid solutions14–21. Earlier studies shown that organic compounds containing heteroatoms such as N, O, S, and others, as well as aromatic rings, work as excellent corrosion-protecting chemicals. The MOF looks to be a potential inhibitor because it mixes of metal ions with an organic framework. The addition of more electropositive metals to the organic framework enhances sacrificial efficacy. The organic structure, on the other hand, forms a protective covering over the metal surface, slowing corrosion. A few studies in the literature22 showed that MOF can be used as an efficient corrosion inhibitor reported a 3D network of silver-based MOFs that were found to be suitable for preventing \(\text{C-steel}\) corrosion in 1 M HCl solution. In another investigation, metal organic frameworks based on both silver and nitrogen donors were shown to be efficient \(\text{Cu}\) corrosion inhibitors in HCl solution23. MOFs with organic ligands comprising substituted aryl, heteroaryl, or heterocyclic compounds with an exocyclic sulphur group have also been described for use as corrosion inhibitors in metals and alloys24. A new MOF from \(\text{Cd}\) has been reported in the literature25. The impact of Co, Ni, and Cu metal–based MOFs on mild steel corrosion prevention was reported in 201726. MOF research has resulted in the use of hydrophobic MOFs like ZIF-8 in the anticorrosion sector27. ZnAl-CO₃ layered double hydroxide precursor buffer layers were transformed to well intergrown ZIF-8 coatings in that study28. A recent research created an anticorrosive coating for the petrochemical...
Table 1. C-steel chemical structure.

| Elements | C  | Mn  | P  | Si  | Fe  |
|----------|----|-----|----|-----|-----|
| Weight % | 0.20 | 0.60 | 0.004 | 0.003 | Rest |

Table 2. Chemical structures of metal–organic compounds (SC1 & SCP2).

| Compound | Mol. formula | Mol. Wt | Structure |
|----------|--------------|---------|-----------|
| SC1      | C16H40Co2N12O7S4 | 774.70 g/mol | \([\text{Co}_2(\text{SCN})_4(\text{hmt})_2(\text{H}_2\text{O})_6.\ H_2\text{O}]\) |
| SCP2     | (C23H35O1N8CoSn3) | 854.64 g/mol | \([\text{Co}_2(\text{SCN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}).\ (\text{qox})]\) |

industry using Samarium (III) nitrate and [bis(phosphonomethyl) amino] methyl phosphonic acid (ATMP) to preserve mild steel in saline solutions. According to a thermodynamic research, the extremely excellent inhibitory property of MOF on metal surface was attributed to chemisorption of MOF on metal surface.

MOFs derived from nanostructures have a higher specific surface area and good form, such as nano cages and hollow spheres, as compared to other nanostructures. This motivated us to investigate the use of SC1 and SCP2 as corrosion inhibitors for C-steel in 0.5 M H_2SO_4 solutions. In this study, we utilized the chemical approach (mass reduction method) and electrochemical methods (potentiodynamic polarization (PP) and electrochemical impedance (EIS)). Attenuated total reflection infrared (ATR-IR) and atomic force microscopy (AFM) were employed to assess the metal–organic and surface morphology of C-steel, respectively.

**Experimental**

**Composition of C-steel samples.** The experiments were performed with C-steel type C1018 with the following: composition (Table 1).

For mass reduction measurements, rectangular specimens with dimensions of 2 × 2x0.2 cm were utilized. The exposed surface area of carbon steel for electrochemical testing was 1 cm².

**Chemicals.** By diluting the stock solution (1 × 10⁻³ M) of these compounds with double distilled water, various inhibitor concentrations (5, 10, 15, 20, and 25 × 10⁻⁶ M) were produced. In 0.5 M H_2SO_4, the maximal soundness of a metal–organic compound was reported to be 25 × 10⁻⁶ M. The metal–organic complex employed in this work is highly soluble in water, has higher molecular weights, and includes a significant number of donating atoms (N and O) and easily available, non-toxic and their structures are listed in Table 2.

**Preparation and characterization of inhibitors.** Preparation of \([\text{Co}_2(\text{SCN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}).\ (\text{qox})]\) (SCP2). In the presence of ultrasonic radiation, red crystals of \([\text{Co}_2(\text{SCN})_4(\text{hmt})_2(\text{H}_2\text{O})_6.\ H_2\text{O}]\) (SC1) were produced. In an ultrasonic bath, a 0.118 g (0.5 mmol) solution of \(\text{CoCl}_2.6\text{H}_2\text{O}\) dissolved in 10-mL bidistilled H₂O was gradually added to a stirred mixture of 0.099 g (0.5 mmol) trimethyl tin chloride and 0.097 g (1 mmol) KSCN in 10 mL of CH₃CN/deionized H₂O. Following a few minutes of magnetic stirring, a solution of 0.07 g hexamethylenetetramine (hmt) in 10 mL H₂O was added to the mixture drop by drop. The resulting mixture was ultrasonically treated for 6 h at 30 °C with a power of 60 W. Filtering, precipitation, washing with 10 mL H₂O, and drying in the open air were then used to separate the precipitate SC1 had been obtained in the amount of 367 mg (94.2 percent). SC1, C₁₆H₄₀Co₂N₁₂O₇S₄, MW = 774.70 g/mol, calculated percent: C, 25.47; H, 5.36; N, 22.15; Co, 15.61; S, 16.97. The beam line in Trieste (Italy) was used to gather single-crystal diffraction data.

Chemical structures of metal–organic compounds (SC1 & SCP2).

| Compound | Structure |
|----------|-----------|
| SC1      | \([\text{Co}_2(\text{SCN})_4(\text{hmt})_2(\text{H}_2\text{O})_6.\ H_2\text{O}]\) |
| SCP2     | \([\text{Co}_2(\text{SCN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}).\ (\text{qox})]\) |

Synthesis of \([\text{Co}_2(\text{CN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}).\ (\text{qox})]\), (SCP2). Self-assembly of the ternary adducts of \(\text{K}_3[\text{Co} (\text{CN})_6]\) [104 mg (0.315 mmol)] in 10 mL H₂O, Me₃SnCl [189 mg (0.95 mmol)] in 10 mL H₂O, and quinoxaline (qox) [41 mg (0.315 mmol)] in 10 mL acetonitrile yields white prismatic crystals. After filtration, washing with small quantity of cold H₂O and acetone and drying overnight, 169 mg (63.3% referred to \(\text{K}_3[\text{Co} (\text{CN})_6]\)) of colorless crystals of SCP2 were obtained. Anal. Calc. for SCP2 (C₂₃H₃₅O₁N₈CoSn₃) MW = 854.64 g mol⁻¹, %: C, 32.32; H, 4.13; N, 13.11; Co, 6.90; Found: C, 32.10; H, 4.01; N, 13.06; Co, 7.03. FT-IR-data (cm⁻¹): 3444 (νH₂O), 2952 (assym.CH), 2279 (sym.CH), 1457 (CH), and (δCH), and 697 (γCH) of thiocyanate, 814 (νCo–N), 426 (νCo–N-hmt). Data for X-ray single crystal diffraction are collected at the Elettra Synchrotron's beam line (XRD1) in Trieste, Italy.

\[\text{K}_3[\text{Co} (\text{CN})_6] + \text{Me}_3\text{SnCl} + \text{quinoxaline} \rightarrow [\text{Co} (\text{CN})_6(\text{Me}_3\text{Sn})_3(\text{H}_2\text{O}).\ (\text{qox})], \text{SCP2}\]
Methods

Mass reduction (MR) tests. The usual technique for measuring the dissolution rate and inhibition efficacy (percent IE) is MR approach in which a 2 × 2 × 0.2 cm² piece of metal is used. The samples are cut and sanded as previously, then washed with double distilled water, dried, and weighed before being placed in solutions made from varying dosages of metal–organic compounds ranging from 5 × 10⁻⁶ to 5 × 10⁻⁶ M in a beaker containing 0.5 M H₂SO₄ and changing quantities of metal–organic compound inhibitors for 3 h. and metal–organic compound inhibitors in varying concentrations for 3 h. This happens in the presence of 0.5 M H₂SO₄ when compared to a sample put in a solution of 0.5 M sulfuric acid without the addition of metal–organic compounds. The samples are weighed before being re-immersed in respective solutions. The temperature varies between 298 and 318 K. After drying thoroughly, for 3 h, it was put in a beaker with 0.5 M H₂SO₄ and varying amounts of metal–organic inhibitors. All experiments were repeated three times for reproducibility.

Electrochemical tests. Measurements of PP. The capacity of PP was adjusted automatically from −700 to +700 mV against (Eocp). At a scan rate of 1 mVs⁻¹, the power was measured.

Measurement of EIS. All open-circuit testing with EIS were carried out with AC signals ranging from 100 kHz to 0.1 Hz and peak amplitudes of 10 mV at open circuit potential (OCP). The equipment used in electrochemical experiments was a “Gamry Potentiostat/Galvanostat/ZRA” (PCI4-G750). Gamry comprises the DC105 DC Corrosion Program, the EIS300 EIS Program, and a data gathering computer. To plot and compute data, Echem Analyst version 5.5 was used”.

Morphology of the surface. Attenuated Total Reflection Infra-Red (ATR-IR) analysis. ATR-IR spectra were recorded in the spectral region “4000 to 500 cm⁻¹” using the Attenuated Total Reflectance (ATR) technique on an FTIR-Spectrometer iS 10. (Thermo Fisher Scientific, USA). The FT-IR spectrum is a useful tool for comparing inhibitor and corrosion products following inhibitor adsorption. After immersion for a period, the FT-IR peak values for metal–organic and C-steel were obtained. After 24 h of immersion in the acid corrosive solution with 25 × 10⁻⁶ M of metal–organic, the peak values of the FT-IR were recorded for metal–organic and C-steel.

Atomic force microscopy (AFM) analysis. AFM is a modified test that provides data on the surface of a C-steel sample with metric linear purity. Persecution is used to apply and appraise measured knowledge. Adapted from the SPM management computer code.

Results data and discussion

Crystal structure of [Co(hmt)₆(NCS)₂(H₂O)₂] {Co(NCS)₂(H₂O)₄(H₂O)} (SC1). Sonochemical synthesis of the quaternary adducts hmt, CoCl₂·6H₂O, Me₃SnCl, and KSCN in CH₃CN/H₂O resulted in red crystals of the tin-free empirical composition [Co₂(SCN)₂(hmt)₂(H₂O)₂]. SC1’s structure displays two unique complexes composed of two crystallographic and chemically distinct Co³⁺ atoms, one hmt molecule, two thiocyanate ligands, three coordinated water ligands, and one H₂O molecule of crystallization (Fig. 1a). SC1’s unit cell structure, on the other hand, consists of two neutral complexes with two different Co³⁺ atoms, four thiocyanate ligands, and one thiocyanate. Two hmt ligands, six coordinated water molecules, and one uncoordinated water molecule (Fig. 1b). The Co1 atom exhibits an octahedral shape based on bond lengths and angles (Table 4, Fig. 1b). The Co–N–C angle shows bent structure (163.93°). To create the OC-6 structure, the Co2 atom coordinates with two thiocyanate groups in apical positions and four water molecules in an equatorial plane geometry, which is maintained by bond lengths and angles (Table 4). The two Co³⁺ components form 1D chains connected by many strong H bonds (1.936–2.077). (See Fig. S1). As seen in Fig. S2, the structure of SC1 extends three dimensions via strong H-bonds. The lattice water molecule and the Co³⁺ fragment, [Co(SCN)(H₂O)₂], are arranged in rows between the chains of [Co(SCN)(hmt)(H₂O)₂], and they are responsible for SC1’s strong backstructure via strong H-bonds (1.911–2.994).

Crystal structure of [3][Co(CN)₃(Me₃Sn)₃(H₂O)(qox)] (SCP2). SCP2’s asymmetric unit is composed of one crystallographically independent Co³⁺ center, six ordered cyanide ligands, three crystallographically distinct Me₃Sn⁺ cations, and one coordinated water molecule, as well as qox as a guest molecule, as shown in Fig. 2, Table S3 (in the supplementary file). The Co³⁺ atom is six coordinated to the carbon end of the six ordered cyanide ligands with Co–C distances in the range of 1.872(5) – 1.884(6) Å, Table S4. Table S4 shows that the C–Co–C angles imply an octahedral shape of the Co³⁺ core. The Co(CN)₃ building blocks are the primary components that make up the host network in that is bridged by the Me₃Sn⁺ cations (in the supplementary file). Tin atoms are coupled to the nitrogen ends of the cyanide groups, resulting in a trigonal bipyramidal structure. Surprisingly, the Sn3 atom has a distinct crystallographic structure than the Sn1 and Sn2 atoms. The Sn3 atom coordinates with three methyl ligands to create the Tp-3 configuration, whereas the N3 atom and one water molecule are located at axial locations, as shown in Fig. 2. As a result, the Me3Sn1 and Me3Sn2 cations act as connectors between the Co(CN)₃ building blocks, resulting in 1D-coordinated chains (Fig. S3), while the Me3Sn3 cation structure ends with an H₂O ligand, which helps in the formation of H-bonds (1.988–3.085) and—stacking (qox–O = 2.771). Surprisingly, five of the cyanide ligands behave as 2-ligands, while the Me3Sn ligand has a free uncoordinated nitrogen end that may make H-bonds with the guest qox molecules (2.703–2.735) and water molecules (2.739). SCP2’s structure propagates three-dimensionally based on infinite, but nonlinearly coordinated –[Co–CN–Sn–NC–Co]– chains that cross each other at quasi-octahedral Co sites, as seen in Fig. S4 (in the supplementary
file). Each qox guest molecule is linked by H-bonds (2.456) and π–π interaction (3.278), and the chains are connected by H-bonds through O1 and C5N5. The 3D-network structure comprises a deformed adamantoid \([\text{Co}_9(\text{CN})_{18}(\text{Me}_3\text{Sn})_9]\) ring, as illustrated in Fig. S5. The network space comprises methyl groups and guest qox molecules in addition to the coordinated water group, resulting in a stunning structure.

Mass reduction (MR) tests. The mass loss which calculated from MR is given by Eq. (1):

$$\Delta W = \frac{W_1 - W_2}{a}$$  \(\text{(1)}\)

\(W_1, W_2\) are the weights of the C-steel specimens before and after reaction with solution.

Equation 2 was used to calculate the IE percentage:

$$\text{IE}\% = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100$$  \(\text{(2)}\)

Table 3. Crystal data and structure refinement parameters of SC 1.

| Chemical formula | C_{16}H_{40}Co_{2}N_{12}O_{7}S_{4} |
|------------------|-----------------------------------|
| Formula weight   | 774.70                            |
| Crystal system   | Triclinic                         |
| Space group      | P-1                               |
|\(a\) (Å)         | 7.8696(16)                        |
|\(b\) (Å)         | 8.9388(18)                        |
|\(c\) (Å)         | 12.827(3)                         |
|\(\alpha\) (°)    | 94.07(3)                          |
|\(\beta\) (°)     | 96.94(3)                          |
|\(\gamma\) (°)    | 114.85(3)                         |
|\(V\) (Å³)        | 805.3(4)                          |
|\(Z\), wavelength | 1, 0.7                            |
|\(\rho_{\text{calc}}\) (g/cm³) | 1.597                             |
| Absorption coefficient, mm⁻¹ | 1.348                             |
|\(F(000)\)        | 402.0                             |
|\(\theta\) range, deg | 1.590°–29.996°                    |
| Index range \(h, k, l\) | 11,12,18                         |
|\(R_{int}\)       | 0.023                             |
| Data/restraint/parameters | 4761/16/226                   |
| Goodness of fit on \(F^2\) | 1.1158                            |
| Final \(R_c, wR_c\) (I > 2σ(I)) | 0.0279, 0.0843                  |
|\(\Delta\rho_{\text{max}}\), \(\Delta\rho_{\text{min}}\) (eÅ⁻³) | 0.58, −0.77                     |
| CCDC NO           | 1991081                           |

Table 4. Bond lengths (Å) and bond angles (deg.) of SC1.

| Bond lengths (Å)                  | Bond angles (deg.)                  |
|-----------------------------------|-------------------------------------|
| Co2—N1                            | 1.166                               |
| Co2—O2                            | 2.065                               |
| Co2—O3                            | 2.106                               |
| N2—C2                             | 1.166                               |
| C2—S2                             | 1.645                               |
| Co2—C2                            | 3.265                               |
| N2—S2                             | 2.811                               |
| CO1—O1                            | 2.088                               |
| CO1—N1                            | 2.051                               |
| CO1—N3                            | 2.305                               |
| N2—C2                             | 178.37                              |
| Co2—N2—C2                         | 177.28                              |
| N1—CO1—O1                         | 90.16                               |

The mass loss which calculated from MR is given by Eq. (1):

$$\Delta W = \frac{W_1 - W_2}{a}$$  \(\text{(1)}\)

\(W_1, W_2\) are the weights of the C-steel specimens before and after reaction with solution.

Equation 2 was used to calculate the IE percentage:

$$\text{IE}\% = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100$$  \(\text{(2)}\)
Figure 1. Asymmetric unit perspective view (a); SC1 structure perspective view using atom labelling technique (b).

Figure 2. (a) ORTEP schematic of SCP2 displaying the atom labelling scheme and thermal ellipsoids with 50% probability (b) Perspective view of the SCP2's asymmetric unit displaying the atom labelling scheme.
where $\Delta W$ and $\Delta W_i$ represent the $MR$ per unit area in the absence and presence of prepared samples, respectively. This measurement was performed in accordance with ASTM standard G 31–72. The $MR$–$time$ curves for C-steel in the presence and absence of changed dosages ranging from $5 \times 10^{-6}$ to $25 \times 10^{-6}$ M for SC1 and SCP2 are shown in Fig. 3. The $k_{corr}$ grew as the temperature increased, therefore the $k_{corr}$ increased while the IE percent decreased. The curves in the presence of inhibitors are lower than those in the absence of inhibitors. The higher IE percent with increased dosage of metal–organic compounds can be attributed to the formation of an inhibitor layer on the C-steel surface via adsorption. This layer is formed by the free electron pairs on the oxygen and nitrogen atoms of metal–organic compound molecules, as well as the $\pi$-electrons of aromatic rings. The reduction in IE percent with rising temperature is most likely due to a higher rate of desorption, which is physical adsorption; the IE percent order was: SC1 > SCP2 Table 5 for example, shows the IE percent and $k_{corr}$ at various dosage of metal–organic SC1 of C-steel at temperatures ranging from 298 to 318 K for 120 min immersion. As seen in the Table, raising the temperature lowers the % IE while raising the inhibitor doses raises it.

**Temperature influence on corrosion procedure.** The activation energy $E_a^*$, which can be derived from Eq. (3), is an essential component that influences the speed of reaction and the kind of adsorption.

$$\log k_{corr} = \log A - E_a^*/2.303RT$$

where $k_{corr}$ is the corrosion rate. Figure 4 depicts Arrhenius diagrams for SC1 and SCP2 [log ($k_{corr}$) versus $1/T$], where the $E_a^*$ energy of the activation of the results was obtained in Table 6. It suggests that the surface reaction dominates the overall activity since the activation corrosion process ($E_a^*$) is more than $20 \text{ kJ mol}^{-1}$ and the activation energy increases as the dosage of metal–organic compound increases. Energy rises as the dose of metal–organic compound increases, it appears that the surface reaction dominates the overall activity. The adsorption nature of metal–organic compounds on C-steel causes this rise, which correlates to the physical adsorption of metal–organic compounds. The transitional state equation was used to calculate the changes in entropy and enthalpy. The activation enthalpy ($\Delta H^*$) and entropy ($\Delta S^*$) increases for C-steel corrosion in 0.5 M H$_2$SO$_4$ are calculated using the equation below:

$$\log (k_{corr}/T) = [\log (R/Nh) + \Delta S_a^*/2.303R] - \Delta H_a^*/2.303RT$$

where symbol “$h$” is the Planck’s constant and $N$ is the Avogadro’s number. Graph of log ($k_{corr}/T$) versus ($1/T$) for unprotected C-steel at 0.5 M H$_2$SO$_4$ and in the existence of metal–organic compounds is shown in Fig. 5, which gave straight lines with slope equal ($-\Delta H^*/2.303R$) and an intercept equal (log $R/Nh - \Delta S^*/2.303R$) from which $\Delta H^*$ and $\Delta S^*$ data were calculated and depicted in Table 6. Negative results for ($\Delta H^*$) on the C-steel surface, indicating that the reaction that occurs during the dissolving process is exothermic, and it is known that they may be used to chemical and physical adsorption and the $\Delta S^*$ is both high and negative, indicating that the activated complex is associated rather than dissociated during the rate-determining stage.

**Adsorption isotherm behavior.** Studding of adsorption isotherms help us to explain the reaction occurred among the C-steel surface and metal–organic additives. It is deduced that $0$ increased with raising the inhibitor dose; this is because of the adsorption of metal–organic additive molecules on the C-steel surface. It is also supposed that the adsorption of the studied metal–organic additives is proceeding with the monolayer adsorption so that the adsorption process may obeys Langmuir isotherm. The $Cinh/relationship$ dependence for
SC1 and SCP2 is shown in Fig. 6, because of the dosage of metal–organic compounds ($C_{inh}$) obeying Langmuir isotherm adsorption.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + \frac{C}{2}$$  \hspace{2cm} (5)

where $K_{ads}$ is the equilibrium adsorption constant intricate in chemical reaction

$$K_{ads} = \left(\frac{1}{55.5}\right)^2 \exp\left(-\Delta G_{ads}^\circ / RT\right).$$ \hspace{2cm} (6)

In which the free adsorbent energy is stimulated by a 55.5 dosage of molar water in solution. The data pattern revealed a negative sign of $\Delta G_{ads}^\circ$ due to the spontaneous and stable adsorbed layer on the metal surface$^{43}$. The adsorption characteristics for the metal–organic compounds found are shown in Table 7. The free energy findings show that the kind of adsorption for SC1 is physical and chemical adsorption but physical in case of SCP2, since it is known that negative values are greater than 20 kJ mol$^{-1}$ and less than 40 kJ mol$^{-1}$ for SC1. The $\Delta G_{ads}^\circ$ values ranged between −22.7 and −23.1 kJ mol$^{-1}$, suggesting physical and chemical adsorption (mixed adsorption), but between 21 anf 21.5 kJ mol$^{-1}$ for SCP2 which showed that it adsorbed on C-steel surface physically.

The enthalpy of adsorption, $\Delta H_{ads}^\circ$, was determined using the Vant Hoff equation:

$$\log K_{ads} = \frac{\Delta H_{ads}^\circ}{2.303RT} + \text{constant}.$$ \hspace{2cm} (7)

Figure 7 shows plotting of $\log K_{ads}$ with $1/T$ for C-steel in 0.5 M H$_2$SO$_4$ with SC1. The negative sign of the $\Delta H_{ads}^\circ$ value indicates that the adsorption process is exothermic. Adsorption can be physical or chemical in an exothermic process, while it can only be chemical in an endothermic process. Finally, the following equation may be used to calculate $\Delta S_{ads}^\circ$.

$$\Delta S_{ads}^\circ = \left(\Delta H_{ads}^\circ - \Delta G_{ads}^\circ\right) / T.$$ \hspace{2cm} (8)

| Conc., × 10$^{-6}$ (M) | Temp (K) | $k_{corr}$ (mg cm$^{-2}$ min$^{-1}$) | $\theta$ | %IE |
|------------------------|-----------|-------------------------------------|--------|-----|
| Blank                  | 298       | 0.10689 ± 0.0020                    | -      | -   |
| 5                      | 0.10759 ± 0.0023 | 0.879                             | 87.0   |     |
| 10                     | 0.01386 ± 0.0018 | 0.889                             | 88.9   |     |
| 15                     | 0.01184 ± 0.0026 | 0.901                             | 90.1   |     |
| 20                     | 0.01062 ± 0.0015 | 0.919                             | 91.9   |     |
| 25                     | 0.00857 ± 0.0021 | 0.926                             | 92.6   |     |
| Blank                  | 303       | 0.13398 ± 0.0013                    | -      | -   |
| 5                      | 0.01976 ± 0.0023 | 0.853                             | 85.3   |     |
| 10                     | 0.01813 ± 0.0021 | 0.865                             | 86.5   |     |
| 15                     | 0.01635 ± 0.0013 | 0.878                             | 87.8   |     |
| 20                     | 0.01501 ± 0.0017 | 0.888                             | 88.8   |     |
| 25                     | 0.01264 ± 0.0018 | 0.906                             | 90.6   |     |
| Blank                  | 308       | 0.19856 ± 0.0021                    | -      | -   |
| 5                      | 0.03263 ± 0.0015 | 0.836                             | 83.6   |     |
| 10                     | 0.02956 ± 0.0012 | 0.851                             | 85.1   |     |
| 15                     | 0.02626 ± 0.0014 | 0.868                             | 86.8   |     |
| 20                     | 0.02406 ± 0.0021 | 0.879                             | 87.9   |     |
| 25                     | 0.0212 ± 0.0020  | 0.893                             | 89.3   |     |
| Blank                  | 313       | 0.26488 ± 0.0019                    | -      | -   |
| 5                      | 0.04826 ± 0.0022 | 0.818                             | 81.8   |     |
| 10                     | 0.04456 ± 0.0017 | 0.832                             | 83.2   |     |
| 15                     | 0.042 ± 0.0023   | 0.841                             | 84.1   |     |
| 20                     | 0.03773 ± 0.0020 | 0.858                             | 85.8   |     |
| 25                     | 0.03175 ± 0.0018 | 0.880                             | 88.0   |     |
| Blank                  | 318       | 0.31742 ± 0.0021                    | -      | -   |
| 5                      | 0.06437 ± 0.0015 | 0.797                             | 79.7   |     |
| 10                     | 0.06208 ± 0.0002 | 0.804                             | 80.4   |     |
| 15                     | 0.05715 ± 0.0023 | 0.820                             | 82.0   |     |
| 20                     | 0.05123 ± 0.0017 | 0.839                             | 83.9   |     |
| 25                     | 0.04368 ± 0.0018 | 0.862                             | 86.2   |     |

Table 5. (%IE) and $k_{corr}$ at various dosages of metal–organic SC1 of C-steel for 120 min immersion at 298–318 K temperature range.
Table 7 shows the values for $\Delta S_{\text{ads}}$. The negative sign of $\Delta S_{\text{ads}}$ values indicates that the order of the adsorbed molecules at the solid/liquid contact is decreasing.

**Electrochemical measurements.** PP measurements. PP diagrams of C-steel in 0.5 M sulfuric acid in the existence and absence of altered doses of metal–organic compounds at 298 K are shown in Fig. 8. From this Figure we see that Tafel extrapolation obtained the electrochemical parameters at $E_{\text{corr}}$ and were depicted in Table 8. The current density reduced as the accumulation of inhibitors increased. According to the results of the tests, $\beta_c$ is somewhat greater than $\beta_a$, suggesting that the inhibitors favor cathodic rather than nodic action. As a result, these inhibitors function like a combination of inhibitors. Also, $E_{\text{corr}}$ change slightly (less than ± 85 mV) which confirm that these compounds exert on both cathodic (hydrogen reduction) and anodic (metal dissolution) processes. The efficacy of inhibition (IE%) was determined from the curves of polarization as in Eq. (9):

$$IE\% = \left(1 - \left(\frac{i_{\text{corr}}}{i_{\text{corr}}^0}\right)\right)$$  \hspace{1cm} (9)
where $i_{corr}$ and $i_\text{corr}^0$, respectively, are the current densities of corrosion with and without of metal–organic compounds (SC1 & SCP2)\(^{44,45}\). The parallel Tafel lines with and without inhibitors indicate that there is no change in corrosion mechanism.

**Electrochemical impedance spectroscopy (EIS) measurements.** Figures 9 and 10 show the C-steel Nyquist and Bode diagrams at OCP in the presence and absence of different dosages of metal–organic SC1 and SCP2 at 298 K. The circuit that represents metal organic compounds and electrolyte is presented in Fig. 11, with $R_s$ as the solution resistance. The impedance spectra show that the diameter decreases as the dose of studied inhibitors rises. The interfacial capacitance $C_{dl}$ values can be estimated from CPE parameters ($Y_0$ and $n$) and is defined in Eq. (10)\(^{46-50}\):

$$C_{dl} = Y_0(\omega_{\text{max}})^n$$

where $Y_0$ is the CPE magnitude, and $n$ is the variance CPE data of the: $-1 < n < 1$. Using Eq. (10). Table 9 shows the impedance data that established the data of $R_{ct}$ increasing with increasing the dosage of the metal–organic compounds.
Table 7. Shows the kinetic characteristics of the studied chemicals as a function of temperature for C-steel dissolving at 0.5 M H₂SO₄ in SC1 and SCP2.

| Inhibitor | Temp. (K) | $K_{ads} (M^{-1})$ | $-\Delta G^{\circ}_{ads} (kJ \ mol^{-1})$ | $-\Delta H^{\circ}_{ads} (kJ \ mol^{-1})$ | $-\Delta S^{\circ}_{ads} (J \ mol^{-1} \ K^{-1})$ |
|-----------|-----------|---------------------|---------------------------------------|----------------------------------------|------------------------------------------|
| SC1       | 298       | 173 ± 0.2309        | 78 ± 0.1735                           | 185 ± 0.2028                           |                                          |
|           | 303       | 157 ± 0.2027        | 78 ± 0.1735                           | 181 ± 0.2333                           |                                          |
|           | 308       | 141 ± 0.2603        | 78 ± 0.1735                           | 178 ± 0.1453                           |                                          |
|           | 313       | 124 ± 0.1732        | 78 ± 0.1735                           | 175 ± 0.1732                           |                                          |
| SCP2      | 298       | 91 ± 0.1764         | 73 ± 0.1413                           | 174 ± 0.2128                           |                                          |
|           | 303       | 81 ± 0.1856         | 73 ± 0.1413                           | 170 ± 0.1764                           |                                          |
|           | 308       | 75 ± 0.1528         | 73 ± 0.1413                           | 167 ± 0.1453                           |                                          |
|           | 313       | 68 ± 0.2646         | 73 ± 0.1413                           | 164 ± 0.2028                           |                                          |

Figure 7. Log $K_{ads}$ versus $T$ diagrams obtained from Langmuir adsorption isotherm for SC1 & SCP2.

Figure 8. PP diagrams for the dissolution of C-steel in 0.5 M H₂SO₄ with and without altered doses of SC1 & SCP2 at 298 K.
compounds, pointing to an increase in IE percent. This might be due to an increase in the thickness of the adsorbed layer caused by increasing the metal–organic compound dosages. The Table also shows that \((n)\) value varies directly with SC1 and SCP2 dosages. \((n)\) value is a measure of surface roughness\(^51\), and its rise might indicate a reduction in the heterogeneity of the metal surface caused by SC1 and SCP2 adsorption. The inclusion of SC1 and SCP2 results in lower \(C_{dl}\) values, which the Helmholtz model ascribed to an increase in the thickness of the electric double layer or/and a drop in the local dielectric constant\(^52\):

\[
C_{dl} = \varepsilon \varepsilon_0 A / \delta \tag{11}
\]

where \(\varepsilon\) is the dielectric constant of the medium, \(\varepsilon_0\) is vacuum permittivity, \(A\) is the electrode area and \(\delta\) is the thickness of the protective layer. Bode graphs (Fig. 11) in the presence of inhibitors revealed that the Bode amplitude value increases over the whole frequency range with the addition of SC1 and SCP2. Equation 12 was used to get the percent IE and \(\theta\) from the impedance testing:

\[
\%IE = \theta \times 100 = \left[ 1 - \frac{R_p^u}{R_p^p} \right] \times 100 \tag{12}
\]

where \(R_p^u\) and \(R_p^p\) are the resistances unprotected and protected metal–organic compounds, individually. Table 10 shows the values of parameters such as \(R_p\) and \(R_c\) obtained from EIS fitting, as well as the derived parameters \(C_{dl}\) and IE percent. The usual criteria for evaluating the best fit of these compounds were followed: the chi-square errors were low \((\chi^2 \approx 10^{-4})\) and the allowable errors of elements in fitting mode were low (5%). As a result, the utilised circuit is acceptable in this situation.

Table 8. Effect of SC1 & SCP2 concentrations on \((E_{corr})\), \((i_{corr})\), \((\beta_c, \beta_a)\), \((\Theta)\) and \((IE\%)\) of C-steel in 0.5 M H\(_2\)SO\(_4\) at 298 K.

| [Inh] | Conc. \(\times 10^6\) (M) | \(-E_{corr}\) mV versus SCE | \(i_{corr}\) (mA cm\(^{-2}\)) | \(\beta_c\) (mVdec\(^{-1}\)) | \(\beta_a\) (mVdec\(^{-1}\)) | \(\theta\) | IE% |
|-------|------------------|-----------------|----------------|----------------|----------------|-------|-----|
| Blank | –                | 410 ± 0.2028    | 0.9327 ± 0.0015 | 267 ± 0.2028 | 145 ± 0.1453 | –     | –   |
| SC1   | 5                | 391 ± 0.1453    | 0.4576 ± 0.0173 | 119 ± 0.1732 | 128 ± 0.2028 | 0.509 | 50.9 |
|       | 10               | 439 ± 0.2431    | 0.3183 ± 0.0260 | 152 ± 0.2309 | 165 ± 0.2906 | 0.659 | 65.9 |
|       | 15               | 435 ± 0.2055    | 0.2574 ± 0.0202 | 97 ± 0.2333  | 113 ± 0.1732 | 0.724 | 72.4 |
|       | 20               | 396 ± 0.1452    | 0.1412 ± 0.0176 | 125 ± 0.1202 | 152 ± 0.2028 | 0.849 | 84.9 |
|       | 25               | 424 ± 0.1742    | 0.0639 ± 0.0202 | 127 ± 0.1732 | 145 ± 0.2082 | 0.931 | 93.1 |
| SCP2  | 5                | 372 ± 0.2102    | 0.4942 ± 0.0173 | 105 ± 0.2333 | 160 ± 0.1732 | 0.470 | 47.0 |
|       | 10               | 427 ± 0.2209    | 0.3866 ± 0.0112 | 114 ± 0.1453 | 154 ± 0.2082 | 0.586 | 58.6 |
|       | 15               | 393 ± 0.2010    | 0.2721 ± 0.0217 | 112 ± 0.2027 | 129 ± 0.1764 | 0.708 | 70.8 |
|       | 20               | 447 ± 0.1753    | 0.1849 ± 0.0231 | 149 ± 0.1764 | 169 ± 0.2082 | 0.802 | 80.2 |
|       | 25               | 358 ± 0.1208    | 0.1057 ± 0.0118 | 101 ± 0.2333 | 156 ± 0.2028 | 0.887 | 88.7 |

Figure 9. Nyquist graphs for C-steel dissolving in 0.5 M H\(_2\)SO\(_4\) in the presence and absence of different dosages of metal–organic SC1 and SCP2 at 298 K.
Figure 10. Bode graphs for C-steel dissolving in 0.5 H₂SO₄ in the presence and absence of different dosages of metal–organic SC1 & SCP2 at 298 K.

Figure 11. Equivalent circuit model used to fit experimental EIS.

Table 9. EIS parameters for the dissolving of C-steel in 0.5 M H₂SO₄ with and without changed dosages of studied metal–organic compounds (SC1&SCP2) at 298 K.

| [Inh] | Conc. × 10⁶ (M) | Rₛ, (Ω cm²) | n | Cₓ, (µF/cm²) | Rₓ, (Ω cm²) | IE% | χ² |
|-------|----------------|-------------|---|--------------|-------------|------|----|
| Blank | – | 1.9283 ± 0.0145 | 0.980 | 586.9 ± 0.1453 | 30.36 ± 0.1453 | – | 0.000082 |
| SCP2 | 5 | 3.3586 ± 0.0239 | 0.985 | 405.7 ± 0.1202 | 66.7 ± 0.1732 | 54.5 | 0.000551 |
| 10 | 3.3075 ± 0.0153 | 0.989 | 326.2 ± 0.2309 | 108.7 ± 0.1453 | 72.1 | 0.000423 |
| 15 | 3.3089 ± 0.0153 | 0.989 | 326.2 ± 0.2309 | 108.7 ± 0.1453 | 72.1 | 0.000423 |
| 20 | 3.3089 ± 0.0153 | 0.989 | 326.2 ± 0.2309 | 108.7 ± 0.1453 | 72.1 | 0.000423 |
| 25 | 3.3089 ± 0.0153 | 0.989 | 326.2 ± 0.2309 | 108.7 ± 0.1453 | 72.1 | 0.000423 |

Table 10. Shows AFM data for the surfaces of SC1 and SCP2 with and without the inhibitor 0.5 M H₂SO₄.
Surface analysis. AFM analysis. AFM in Table 10 and Fig. 12 measured the surface roughness of C-steel in 0.5 M H2SO4 in the presence and absence of 25 × 10^{-6} M. Where, (a) shows blank, (b) C-steel free (c) C-steel with SC1 and SCP2 at 25 × 10^{-6} M.

The roughness calculated from AFM image are summarized in Table 10. The values displayed that the roughness rises with adding H2SO4 due to the corrosion occurs on the C-steel surface but decreased with adding the prepared.

FT-IR analysis. Fourier transform infrared spectroscopy (FT-IR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. "FT-IR spectrum of the corrosion product at C-steel surface in 0.5 M H2SO4 does not show any useful adsorption peaks. FT-IR fingerprint spectra of the stock metal–organic SC1 and the C-steel surface after dipping in 0.5 M H2SO4 + 25 × 10^{-6} M of metal–organic SC1 for 24 h was obtained and compared to each other it was obviously clear that the same fingerprint of metal–organic SC1 solution present on C-steel surface except the absence of some functional group and it suggested to be due to reaction with H2SO4. From Fig. 13 there are small shift in the peaks at C-steel surface from the original peak of the stock inhibitor solution, these shifts indicate that there is interaction between C-steel and metal–organic (SC1&SCP2).

Corrosion inhibition mechanism analysis. Metal–organic compound inhibitors prevent C-steel corrosion primarily by adsorption on the C-steel surface, where it moves H2O molecules, forming a tight barrier layer. Adsorption is related to inhibitor functional groups such as O, N and S, as well as the potential electronic density and steric effect of active centers, which can donate their lone electron to the d-orbital of Fe, forming a chemical bond that is characteristic of chemical adsorption as in case of SC1 and this confirmed from the values of ΔG^{\text{ads}} which are more than 20 kJ mol^{-1}. On the other hand, the surface of the C-steel sample is positively charge in aqueous acid solution. The SO_{4}^{2-} ions get adsorbed on C-steel sample and turn it as negatively charged surface, the protonated inhibitor metal–organic molecules (cationic) get adsorbed on the negatively charged metal surface by an electrostatic attraction. The protonated molecules may adsorb on C-steel samples, resulting in physi-
cal adsorption (Fig. 14) also confirmed from the values of $\Delta G_{\text{ads}}$ which are about 20 kJ mol$^{-1}$. The order of percent IE is as follows: SC1 (93.1%) > SCP2 (88.7%). This due to the presence of more donating atoms (12 N, 7 O and 4 S) in SC1 than in SCP2 (8 N and 1 O).

**Conclusions**

The metal–organic compounds investigated have a high inhibition efficiency ranging from 93.1 to 91.2% at $25 \times 10^{-6}$ based on measurements of mass reduction as it gives linear variation of mass reduction over time. Electrochemical measurements also provide high inhibition efficiency as Tafel lines moved to higher potential regions and the EIS analysis showed a rise in $R_{\text{ct}}$ and a lowered in $C_{\text{dl}}$ as the dose of the inhibitors improved. The investigated compounds adsorption obeyed Langmuir isotherm. Thermodynamic and kinetic parameters indicated that the metal–organic compound act as mixed kind as the adsorption is spontaneous and involving physical adsorption.

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**Author contributions**
A.B. Wrote the main manuscript text, C., prepared Figures and does the experimental work, All authors reviewed the manuscript.

**Competing interests**
The authors declare no competing interests.

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