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# Computational examination of transition metal-salen complexes for the reduction of $CO_2$

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ARTICLE INFO	A B S T R A C T			
Keywords: CO <sub>2</sub> reduction Density functional theory Electrochemistry	In this comprehensive study, we investigated the catalytic potential of seven transition metal-salen (TM-salen) complexes for the reduction of carbon dioxide ( $CO_2$ ) using <i>ab initio</i> methods. Our findings revealed distinct catalytic behavior among the TM-salen complexes, driven by their electronic and geometric properties. The reduction of hydrogen to H <sub>2</sub> was most favorable on Mn-salen and Cu-salen complexes, indicating potential competition with $CO_2$ reduction. Notably, later TM-salen complexes (Co, Ni, Cu, Zn) exhibited higher energy requirements for the initial $CO_2$ reduction, whereas Mn- and Fe-salen complexes demonstrated potential controlled selectivity, favoring $CO_2$ reduction beyond HCOOH at specific thresholds. Our results highlight Cr-salen and Fe-salen complexes as promising candidates for the $CO_2$ reduction reaction ( $CO_2RR$ ) catalysts due to their reduced competition with hydrogen reduction and low limiting potentials for $CO_2$ reduction. Furthermore, the distinct reaction profiles of TM-salen complexes offer valuable insights for the design and development of efficient catalysts for sustainable $CO_2$ conversion and other chemical transformations. These findings provide a foundation for further exploration and optimization of TM-salen complexes as viable catalysts in environmental and energy-related applications.			

# Introduction

The utilization and conversion of CO<sub>2</sub> into value-added products and feedstock materials represent a promising strategy for mitigating the accumulation of greenhouse gases in Earth's atmosphere, aligning with objectives outlined in the Paris Climate Accord [1]. Presently, a substantial portion of the feedstock material utilized globally is derived from petroleum-based sources necessitating the exploration of alternative production methods to reduce reliance on carbon-intensive sources. One such approach involves the electrochemical reduction of CO<sub>2</sub> using either molecular or surface-based catalysts [2–5]. These catalysts offer distinctive advantages, as they can influence the product distribution and selectivity of reduced CO<sub>2</sub> species or lower the energy barriers associated with the sluggish kinetics of these electrochemical processes.

Molecular catalysts employed for  $CO_2$  reduction typically exhibit enhanced selectivity compared to inorganic, surface-based catalysts owing to their well-defined active sites but often suffer from reduced activity [6]. This phenomenon is frequently attributed to a lower charge density, resulting in weaker  $CO_2$  interactions with the catalyst material, leading to a decreased catalytic efficiency [7]. A wide variety of molecular catalysts have demonstrated successful CO<sub>2</sub> reduction to diverse products, including carbon monoxide (CO), formic acid (HCOOH), methane (CH<sub>4</sub>), and other, higher C<sub>2+</sub> hydrocarbons and oxygenates such ethane, ethanol, or acetic acid [8–12]. These transformations have been achieved using numerous different ligand scaffolds and metal centers.

To gain a deeper understanding of the specific effects arising from the choice of ligand scaffold or metal center on  $CO_2$  reduction capabilities, certain aspects of the systems must be held constant. This can be achieved by either modifying the ligand scaffold while keeping the metal center fixed or by employing a single ligand scaffold while investigating how different metal centers influence the reaction mechanism. Prior experimental work has explored the former approach, examining Co- [13] and Pb-based [14] molecular catalysts with various ligand scaffold modifications. Similarly, studies utilizing a single ligand scaffold with different metal centers have been conducted, revealing varying degrees of impact. For example, Chen et al. [15] demonstrated how changing the metal center of a pentadentate  $N_5$  ligand from Co(II) to Fe(III) selectively controlled the formation of either HCOOH or CO. In another study, Singh et al. [16] observed a three-fold increase in the

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Received 3 November 2023; Received in revised form 19 December 2023; Accepted 2 January 2024 Available online 9 February 2024 2468-8231/© 2024 Published by Elsevier B.V. total Faradaic efficiency for  $CO_2$  reduction using a salphen ligand by changing the metal center from Cu(II) to Ni(II).

By substituting the metal center in a metal-ligand complex, an insightful investigation into the changes in the reaction mechanism of  $CO_2$  reduction driven by the differences in the electronic structure of the metal center can be achieved. Computational methods are well-suited to explore such processes, particularly for simple metal-ligand systems. Through an analysis of the evolving reduction steps as a function of the metal center, an optimal choice for the metal center can be discerned. In this work, we present a computational study employing TM-salen complexes and density functional theory (DFT) to explore  $CO_2$  reduction. TM-salen are particularly well-suited for investigating  $CO_2$  reduction owing to the presence of an open metal site and  $\pi$  conjugation, which facilitates charge transfer [17]. Prior experimental studies on analogous TM-salphen complexes have demonstrated their activity in reducing  $CO_2$  into both  $C_1$  and C2 products, utilizing slightly different functionalized ligand scaffolds and metal centers [14,18,16,19].

While the salphen and salen ligands share the same N<sub>2</sub>O<sub>2</sub> binding site, we anticipate subtle differences in their reactivity. Previous work has shown the utility of a Sb(III)-salen ligand towards HER and so we expect similar electrocatalytic capabilities for the TM-salen complexes [20]. For this study, we focus on TM-salen complexes due to their smaller size and ease of computation, reserving the investigation of metal-salphen complexes for future endeavors. The salen ligand offers several advantages for examining CO2 reduction, including its ability to chelate both small [21] and large [14] metal cations in varying oxidation states, as well as its relative ease of functionalization [22]. Accordingly, we select earth-abundant, 3d transition metals with readily accessible +2 oxidation states: Cr, Mn, Fe, Co, Ni, Cu, and Zn. The air-sensitivity of some of the TM-salen complexes may hinder their use as CO2 reduction catalysts but previous examples in the literature indicate a high likelihood of their stability in the +2 oxidation state [23, 11,24] including recent work by Zhang et al. who were able to incorporate Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) cations into a salen-COF for hydrogen evolution [25]. Additionally, we performed preliminary calculations with Mn-, Fe-, and Co-salen in the +3 oxidation state based on the work of Williams et al. [20] that showed much lower limiting potentials for hydrogen reduction, thus lowering their selectivity for CO<sub>2</sub> reduction. Furthermore, the diverse transition metals afford an opportunity to finely examine how subtle modifications in the electronic structure of the metal center influence the CO<sub>2</sub> reduction reaction. The TM-salen complexes may be synthesized following Fig. 1, wherein ethylenediamine and salicylaldehyde are employed to produce the salen ligand. Subsequently, metals ions are incorporated into the ligand using metal salts such as CuCl<sub>2</sub> or NiCl<sub>2</sub> to complete the formation of the complex.

This work is structured as follows: we begin by presenting our results on the geometric properties of the TM-salen complexes followed by an analysis of the reduction of hydrogen to form H<sub>2</sub> through a protoncoupled electron transfer (PCET) mechanism [26], assessing the energetic differences among the TM-salen complexes. This allows for a succinct exploration of the hydrogen evolution reaction (HER) mechanism on the TM-salen complexes which often competes with CO<sub>2</sub>RR. Next, we examine the CO<sub>2</sub> reduction on the TM-salen complexes, comparing limiting potential values and scrutinizing distinctive reaction pathways to gain insights into which TM-salen complexes are more likely to favorably reduce CO<sub>2</sub>. Based on this comparative analysis, we then discuss the suitability of Cr-, Mn-, and Fe-salen complexes as potential  $CO_2$  reduction catalysts, particularly for the selective production of HCOOH at low applied voltages. Finally, we present our concluding remarks regarding the utility of TM-salen complexes for  $CO_2RR$ .

#### **Computational details**

In this study, we adopt a computational protocol similar to that of previous electrochemical studies [20,27,28,29] employing the B3LYP [30–32] density functional as implemented in the ORCA 5.0.3 software package [33]. The TM-salen complex shown in Fig. 2 is utilized. Standard optimization and SCF convergence criteria are applied, and an unrestricted, Kohn-Sham wave function is assumed for all calculations. Multiple spin states are explored for each metal-salen complex to identify the minimum energy spin state (Table 1). Transition metal atoms are assigned the def2-TZVPP basis set, while all other atoms are assigned the def2-TZVP basis [34]. The Resolution of Identity Chain-of-Spheres (RIJCOSX) [35] algorithm is used to accelerate the calculation of all four-index integrals using the def2/J auxiliary basis set [36]. Dispersion effects are accounted for using the D3 method along with the Becke-Johnson damping factor (D3BJ) [37,38].

Analytical frequency calculations are performed to ensure the validity that optimized structures correspond to minima on the potential energy surface. Solvation effects are considered using the conductor-like polarizable continuum model (CPCM) with dichloromethane (DCM) as the chosen solvent [39]. After optimization in the gas-phase, a single-point calculation using CPCM is performed at the optimized geometry to account for solvation effects. The total energy ( $G_{CPCM}$ ) of each reactant, intermediate, and product is calculated according to Eq. (1) where E represents the total electronic energy, ZPE corresponds to the correction due to zero-point energy and thermal effects, TS denotes the entropy correction,  $\Delta E_{CPCM}$  signifies the energy correction due to solvation effects, and eU is the effect of an applied potential (U) per electron (e). Each reduction step is assumed to follow a proton-coupled electron transfer mechanism, essentially involving the addition of a hydrogen atom to the system to conserve the overall charge of each complex [26, 40]. The electrochemical reaction energies are referenced relative to the reactants, which include the TM-salen complex, a CO2 molecule, and up to eight H+/e- pairs representing the PCET steps. The energy of the reactant, intermediate, and product molecules are calculated using the same computational methodology presented above as singular molecules, while the energy of a single H+/e- pair is set to 1/2 H<sub>2</sub> following the computational hydrogen electrode [41]. The limiting potential is calculated based on the maximum difference between elementary reduction steps ( $\Delta G_{max}$ ). The step at which  $\Delta G_{max}$  occurs for each product (CO, HCOOH, CH<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>4</sub>) is the limiting potential step.



Fig. 2. Structure of the TM-salen complex used in this work. X = Cr(II), Mn(II), Fe(II), Co(II), Ni(II),.



Fig. 1. Formation of the salen ligand from the reaction of ethylenediamine and salicylaldehyde.

#### Table 1

Relative spin state free energies for the TM-salen complexes in the gas-phase. The values are given kcal/mol.

	S = 0	S=1/2	S = 1	S = 3/2	S=2	S = 5/2
Cr	-	-	24.98	-	0.00	-
Mn	-	28.81	-	6.19	-	0.00
Fe	32.46	-	3.48	-	0.00	-
Со	_	0.00	-	4.59	-	-
Ni	0.00	-	7.96	-	-	-
Cu	-	0.00	-	-	-	-
Zn	0.00	-	-	-	-	-

$$G_{CPCM} = E + ZPE - TS + \Delta E_{CPCM} + eU$$
<sup>(1)</sup>

In summary, our computational study employs a robust methodology to investigate the catalytic performance of TM-salen complexes for  $CO_2$ reduction. The theoretical insights gained from this investigation contribute to a comprehensive understanding of the reduction mechanism and provide essential information for identifying suitable TM-salen complexes as potential catalysts for carbon dioxide reduction.

#### Results

The TM-salen complexes demonstrate a conspicuous trend in their lowest energy spin state configurations, exhibiting a preference for highspin configurations among the mid-transition metals Cr, Mn, and Fe, while favoring low-spin configurations for the later metals Co, Ni, Cu, and Zn (Table 1). This phenomenon can be attributed to orbital interactions arising from the square-planar geometry of the TM-salen complexes. Notably, the electronic structure change from Fe to Co facilitates the double occupation of  $d_{xz}$ ,  $d_{yz}$ , and  $d_{z^2}$  orbitals, rather than maximizing the total spin. The selection of high- or low-spin configurations significantly impacts the performance of the TM-salen complexes for CO<sub>2</sub> reduction, as discussed in further detail below.

Upon examining the geometric properties of the TM-salen complexes, notable distinctions emerge in the metal-ligand bond lengths and the ligand O-N-N-O dihedral angle (Table 2, Figure S1). Particularly, the anisotropy between the TM-O and TM-N bond lengths, along with the magnitude of the O—N-N—O dihedral angle, offers valuable insights into the strain experienced by the TM-salen complexes following metal incorporation. TM-complexes that are under strain may exhibit enhanced CO<sub>2</sub> reduction, as the reduced intermediates may be closer in energy, in contrast to less strained, more stable complexes, which may necessitate a higher energetic input to participate in CO<sub>2</sub> reduction. The Mn-, Fe-, and Zn-salen complexes show the most substantial bond anisotropy (0.236 Å, 0.217 Å, and 0.142 Å, respectively), while the Mnsalen and Zn-salen display the largest O-N-N-O dihedral angles of 32.7° and 38.3°, respectively. These observations suggest that the Mn-, Fe-, and Zn-salen complexes might showcase reduced stability, thereby potentially resulting in a more favorable CO<sub>2</sub> reduction process.

To gain insight into the strained nature of the TM-salen complexes, we performed molecular dynamics (MD) simulations using the density functional tight binding (DFTB) [42]. The resulting data in Table S1

#### Table 2

Geometric properties of the TM-Salen complexes. The bonds lengths (R) are averaged between the two O or N atoms and are reported in Å. The dihedral angles ( $\Theta$ ) are given in degrees.

	$R_{TM-O}$	$R_{TM-N}$	$\Delta_{R_{TM-O}-R_{TM-N}}$	$\Theta_{O-N-N-O}$
Cr	1.953	2.036	0.082	4.3
Mn	1.958	2.194	0.236	32.7
Fe	1.923	2.141	0.217	12.0
Co	1.864	1.884	0.021	11.3
Ni	1.855	1.868	0.013	8.9
Cu	1.917	1.969	0.052	12.6
Zn	1.927	2.070	0.142	38.3

presents the average and standard deviation values of the TM-O and TM-N bond lengths over a 50.0 ps trajectory at 350 K. The Mn-, Fe-, and Zn-salen complexes demonstrated the most substantial deviations between the equilibrium bond lengths. Such observations suggest that the potential energy surface of the more strained TM-salen complexes may exhibit a shallower landscape compared to the other complexes, potentially affording greater access to higher energy structures. Such a characteristic could potentially render  $CO_2$  reduction more favorable within these strained TM-salen complexes. No demetalation was observed during the MD simulations which indicate the stability of the TM-salen complexes up to 350 K.

The hydrogen reduction process on the TM-salen complexes comprises two PCET steps wherein the first step can attack either the O or N atoms of the salen ligand scaffold [20] or directly interact with the TM center, leading to the eventual formation of H<sub>2</sub>. As depicted in Fig. 3, the Mn-salen complex exhibits three distinct hydrogen adducts, while Figure S2 showcases the adducts for all seven of the TM-salen complexes. Notably, the NH adduct exhibits the largest change in geometry, transitioning from trigonal planar to tetrahedral, to accommodate the hydrogen atom, whereas the OH and MnH adducts do not involve such large geometry changes. The unique electronic structure of the different TM-salen complexes contribute to the variation in reaction free energies, as shown in Fig. 4. Among the middle TM-salen complexes, the formation of a metal-hydride (green bars in Fig. 4) proves to be the most favorable, while the same adduct is the least favorable for the later complexes. For instance, the Ni-salen exhibits a slightly higher propensity towards forming an OH adduct, while the Cu- and Zn-salen complexes preferentially form NH adducts. In evaluating the limiting potentials potential values for H2 production, the Cu- and Mn-salen complexes demonstrate the smallest values (0.50 eV and 0.69 eV, respectively), while the Cr-, Zn-, and Fe-salen complexes display higher limiting potentials (1.31 eV, 1.07 eV, and 1.03 eV, respectively). Based on these findings, the Cu- or Mn-salen complexes appear to be more suitable candidates for H2 production applications, whereas the Cr-, Zn-, and Fe-salen complexes may offer less competition for CO<sub>2</sub> reduction, making them potentially better suited for this reaction.

The CO<sub>2</sub> reduction reaction involves up to eight PCET steps, potentially yielding five different products: CO, HCOOH, H<sub>2</sub>CO (formaldehyde), CH<sub>3</sub>OH (methanol), and CH<sub>4</sub>. In the initial PCET step, the attack of either the C atom or distal O atom of CO<sub>2</sub> results in the formation of \*OCHO and \*OCOH intermediates, respectively (see Figs. 5, S3). The \*OCOH intermediate is more favorably formed only on the Co- and Cusalen complexes, while the other TM-salen complexes exhibit a preference for the formation of the \*OCHO intermediate. Other intermediates were considered such as those studied by Liu et al. [43] but the geometry of the open-metal site in the TM-salen complexes precludes their formation. Fig. 6 highlights the reaction free energies for these intermediates, revealing the significant difference in energy among the Cr-, Mn-, and Fe-salen complex, which influences the selectivity of product formation. Moreover, Fig. 6 also illustrates the larger energy requirements for the reduction of CO<sub>2</sub> on the later TM-salen complexes, possibly explaining the substantial applied voltages needs for CO2 reduction on similar Ni- and Cu-salphen complexes (1.6-2.0 V vs. SHE) [18,16]. The favorability of the \*OCOH intermediate suggests that only the Co- and Cu-salen complexes would yield appreciable quantities of CO, as the \*OCHO intermediate precludes the formation of CO.

The second PCET step can give rise to five different intermediates (\*CO &  $H_2O$ , \*HOCOH, \*OCH<sub>2</sub>O, \*HCOOH, and \*O &  $H_2CO$ , Figs. 7, S4-S8), but only the closed shell intermediates CO and HCOOH are energetically favorable (green and olive colored bars in Fig. 6). At this stage of the reaction, the Cr-, Mn-, Fe-, Ni-, and Zn-salen complexes are expected to yield only \*HCOOH, while the Co- and Cu-salen complexes are anticipated to form both \*CO and \*HCOOH due to the similar reaction free energies. The oxophilic nature of the middle TM-salen complexes is evident from the smaller energetic penalty associated with the formation of the \*O intermediates compared to the later transition metals, which



Fig. 3. Structures of the a) NH, b) OH, and c) MnH adducts that form on the Mn-salen complex. Color code: white - H, grey - C, blue - N, red - O, black - Mn.



**Fig. 4.** Free energy values for the formation of a hydrogen adduct on the TMsalen complexes. Red bars denote an OH adduct has been formed, blue bars denote an NH adduct form, and green bars denote an XH adduct has formed where X is a transition metal.

exhibit reduced oxophilicity [44]. Additionally, the significant energetic differences between the five possible intermediates further enable selective control of the CO<sub>2</sub> reduction reaction on the TM-salen complexes, favoring the formation of either \*CO or \*HCOOH. The limiting potentials for the  $2e^-$  products indicate that CO<sub>2</sub> reduction would occur with smaller applied potentials using the Cr-, Mn-, Fe-, and Co-salen complexes (0.53 eV, 0.33 eV, 0.25 eV, and 0.81 eV, respectively) compared to the Ni-, Cu-, or Zn-salen complexes (1.78 eV, 1.86 eV, and 1.39 eV, respectively). Therefore, we will focus on the middle TM-salen complexes that are expected to reduce CO<sub>2</sub> to more highly reduced products with lower limiting potentials.

The reduction of CO2 on the Mn- and Fe-salen complexes follows a similar pathway. Fig. 8 illustrates the successive PCET steps involved in the alternate reductions of the C and O atoms of the reduced CO2 intermediates, leading to the formation of CH4 through the formation of the \*OH intermediate. Notably, the two TM-salen complexes exhibit distinct limiting potentials potential values for HCOOH and CH4 formation, which may result in differences in their reduced product profiles depending on the magnitude of the applied potential. At low applied potentials (below 0.53 eV and 0.44 eV for Fe- and Mn-salen, respectively), there is insufficient energy to reduce CO<sub>2</sub> beyond the 2e<sup>-</sup> product HCOOH, as indicated in the blue pathways of Fig. 8. The third PCET step, reducing \*HCOOH to \*HOCH<sub>2</sub>O, is not thermodynamically favorable at these low applied potentials. Instead, this reduction may only occur following an increase in the applied potential to 0.53 eV and 0.44 eV for Mn- and Fe-salen, respectively. Considering this behavior and the free binding energies of the products, different product distributions are expected at different applied potentials. At low applied

potentials, the only anticipated product would be HCOOH, while higher applied potentials would lead to the production of either  $CH_3OH$  or  $CH_4$ . Notably, the \* $CH_3OH$  intermediate is strongly adsorbed to the surface of the Mn-salen complex, promoting the complete reduction to  $CH_4$ . In contrast, the Fe-salen complex is expected to yield appreciable quantities of both  $CH_3OH$  and  $CH_4$  due to a weaker binding of \* $CH_3OH$ . (Fig. 9)

The Cr-salen complex exhibits a slightly different reaction profile compared to the Mn- and Fe-salen complexes during the reduction of CO<sub>2</sub>. While the reduction steps remain nearly the same, the formation of \*H<sub>2</sub>COH is found to be more energetically favorable than the formation of \*CH<sub>3</sub>O (Fig. 10). Additionally, the limiting potentials for HCOOH, H<sub>2</sub>CO, CH<sub>3</sub>OH, and CH<sub>4</sub> formation are all equal (0.54 eV), which restricts the potential-mediated selectivity seen in the Mn- and Fe-salen complexes. As a consequence, the Cr-salen complex is anticipated to produce fewer highly reduced products due to a weak binding of HCOOH. This limitation restricts the occurrence of further reduction steps, ultimately reducing the opportunity for the formation of more highly reduced products like CH<sub>3</sub>OH and CH<sub>4</sub>.

The Co-salen complex exhibits a markedly different reaction profile compared to the previous TM-salen complexes. Notably, the Co-salen complex favors the formation of the \*OCOH intermediate, in contrast to the \*OCHO intermediate observed for the Cr-, Mn-, and Fe-salen complexes. As a result of this behavior, the Co-salen complex is expected to equally produce CO and HCOOH, owing to their similar reaction free energies of 0.50 eV and 0.55 eV, respectively. However, the binding of these products is quite weak, limiting the Co-salen complex's participation in reductions beyond the 2e<sup>-</sup> products. Recent work by Kong et al. on similar Co complexes indicates that CO would be the predominate product for Co-salen over a mixture of HCOOH and CO [45].

#### Discussion

The findings of this study demonstrate significant variations in the performance of the TM-salen catalysts for  $CO_2$  reduction, particularly between the middle and later transition metals. The reduction of hydrogen is expected to dominate for the later transition metals, attributed to their lower limiting potentials and less favorable  $CO_2$  reduction. Specifically, the difference in limiting potentials values between H<sub>2</sub> and HCOOH is -0.86 eV, -1.36 eV, and -0.32 eV for the Ni-, Cu-, and Zn-salen complexes, respectively. The Cu-salen complex in particular is expected to favorably reduce hydrogen, while only exhibiting  $CO_2$  reduction at significantly higher applied potentials.



Fig. 5. Structures of the a) \*OCHO and b) \*OCOH intermediates that form on the Co-salen complex. Color code: white - H, grey - C, blue - N, red - O, pink - Co.



**Fig. 6.** Reaction free energies for the CO<sub>2</sub> reduction reaction on the TM-salen complexes. Upper plot displays the \*OCOH (blue) and \*OCHO (orange) intermediates. Lower plot displays the \*CO (green), \*HOCOH (red), \*OCH<sub>2</sub>O (purple), \*HCOOH (olive), and \*O (grey) intermediates.



Fig. 7. Structures of the a) \*CO, b) \*HCOOH, c) \*OCH2O, d) \*HOCOH, and e) \*O intermediates that form on the Fe-salen complex. Color code: white - H, grey - C, blue - N, red - O, gold – Fe.

Conversely, the middle transition metals are expected to more favorably reduce  $CO_2$ , with limiting potentials differences of 0.78 eV, 0.36 eV, and 0.78 eV on the Cr-, Mn-, and Fe-salen surfaces, respectively, for H<sub>2</sub> and HCOOH. Consequently, we conclude that the middle TM-salen complexes are promising candidates as ideal  $CO_2$  reduction catalysts, surpassing the performance of the later transition metal complexes in this specific application.

An investigation into the bonding orbitals between the TM atoms and the O/N atoms within the salen framework reveals a discernible trend that may elucidate the superior catalytic performance observed in the middle TM-salen complexes. Using the Pipek-Mezey orbital localization scheme [46] and IboView [47,48], we examined the bonding characteristics of TM-N/O bonds concerning the respective transition metals. Our analysis demonstrates a progressive increase in TM character within the TM-N/O molecular orbitals, transitioning from 7 %–9 % from Cr-salen to 16 %–17 % for Zn-salen, while the O/N character decreases from 85 %–90 % to 77 %–81 % across the series (Table 3). The range of values is due to the differences between the O and N atoms of the salen framework.

Primarily O/N in nature for all TM-salen complexes, these orbitals exhibit a distinctive tendency for higher electron acceptance from the N/ O atoms in the salen framework among complexes with fewer d electrons. Conversely, complexes with more d electrons showcase increased back donation from the TM atoms. This elevated back donation might contribute to the stability of the TM-salen complexes, lowering their propensity in reduction reactions. Our MD simulations, as depicted in Table 2, confirm this stability, with the exception of Zn-salen, displaying notable deviations from the DFT optimized geometry due to its closed shell d<sup>10</sup> configuration, leading to comparatively weaker ligand-metal binding.



Fig. 8. Reaction mechanism for the reduction of CO2 on the a) Mn-salen and b) Fe-salen complexes. Free energies given in eV.

The intricacies of this electron donation are currently under investigation within our research group, where we are exploring an expanded range of TM-salphen complexes to comprehensively understand the structure-function relationship in CO<sub>2</sub> reduction. This behavior, coupled with the shift from high-spin to low-spin complexes observed between the Fe-salen and Co-salen, might underpin the superior catalytic performance observed in the middle TM-salen complexes. Notably, similar spin-state regulatory mechanisms have been documented in analogous Co complexes studied by Kong et al. [45].

# Conclusion

In this study, we employed ab initio methods to investigate the potential of seven TM-salen complexes as catalysts for  $CO_2$  reduction. Among them, the Mn- and Cu-salen complexes demonstrated the most favorable reduction of hydrogen to H<sub>2</sub>, showing low limiting potentials values of 0.69 eV and 0.50 eV, respectively. However, this favorable hydrogen reduction is expected to lead to significant competition with  $CO_2$  reduction, thus limiting their feasibility as selective  $CO_2$  reduction catalysts. Notably, later TM-salen complexes, such as those containing Co, Ni, Cu, or Zn, exhibited higher energy requirements for the initial reduction of CO<sub>2</sub>. To gain deeper insights, we focused on the reaction profiles of Cr-, Mn-, and Fe-salen complexes, revealing potentialmediated selectivity with the latter two complexes. For the Mn- and Fe-salen complexes, surpassing a specific threshold potential (0.53 eV and 0.44 eV, respectively) was necessary to produce reduced products beyond that of HCOOH. Based on our comprehensive analysis, Cr-salen and Fe-salen complexes were identified as promising candidates for CO<sub>2</sub>RR due to their reduced competition from hydrogen reduction and small limiting potentials values for CO<sub>2</sub> reduction. These findings open new avenues for further exploration and development of efficient catalysts for sustainable CO<sub>2</sub> conversion and related applications.

#### **CRediT** authorship contribution statement

Gavin A. McCarver: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. Taner Yildirim: Project administration, Resources, Supervision. Wei Zhou: Project administration, Resources, Supervision.



Fig. 9. a) \*CO<sub>2</sub>, b) \*OCOH, c) \*HCOOH, d) \*HOCH<sub>2</sub>O, e) \*H<sub>2</sub>CO, f) \*CH<sub>3</sub>O, g) \*CH<sub>3</sub>OH, h) \*OH, and i) \*H<sub>2</sub>O reaction intermediates for the reduction of CO<sub>2</sub> on the Mn-salen complex. Color code: white - H, grey - C, blue - N, red - O, black - Mn.



Fig. 10. Reaction mechanism for the reduction of CO<sub>2</sub> on the Cr-salen complex. Free energies given in eV.

## Table 3

Percent atomic character of the bonding molecular orbitals between the N/O atoms of the salen framework and TM atoms. Values are based on Pipek-Mezey localized orbitals and were determined using IboView.

	TM-O		TM-N	
	0	TM	N	TM
Cr	89	7	85	9
Mn	90	7	85	8
Fe	88	9	85	9
Со	87	9	83	13
Ni	85	11	81	14
Cu	84	13	81	14
Zn	81	16	77	17

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2024.113819.

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