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Crystallographic data for [Ru(tptz)(CH₃CN)Cl₂]·CH₃CN·0.68H₂O have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1446155.

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Abstract

A new polypyridyl Ru(II) complex, [Ru(tptz)(CH₃CN)Cl₂] (tptz = 2,4,6-tri(2-pyridyl)-1,3,5-triazine) has been prepared and characterized. It crystallizes with one molecule of acetonitrile and a partly occupied water solvent molecule. X-ray analysis of the complex revealed that the central Ru(II) atom has a distorted octahedral Cl₂N₃N' coordination environment. The complex was used as an electrocatalyst for the reduction of CO₂ to CO in an acetonitrile solution as monitored by cyclic voltammetry. The electrocatalytic activity of the complex was investigated for CO₂ reduction under different reaction conditions. The results show that the CO₂ reduction peak current increases with increasing concentration of the electrocatalyst from 0.5 to 2 mM, increasing purging time of CO₂ from 5 to 30 min, and increasing scan rate from 0.1 to 0.5 V s⁻¹. The catalytic activity of the Ru(II) complex is decreased at lower temperatures because of the relationship between the activation energy and temperature. The suggested electrocatalytic mechanism was confirmed by computational studies. The calculations indicate that the electrocatalytic mechanism includes six steps. The electrocatalyst undergoes two sequential one-electron tptz-based reductions followed by

substitution of the CH_3CN by CO_2 to yield a metallocarboxylate intermediate. This intermediate ($\text{Ru}^{\text{II}}(\eta^1\text{-CO}_2^{2-})$) is involved in further tptz-based reductions and an oxide (O^{2-}) transfer to the free CO_2 to yield a monocarbonyl Ru(II) complex ($[\text{Ru}^{\text{II}}(\text{tptz}^{2-})(\text{CO})\text{Cl}_2]^{2-}$) and the carbonate anion. The monocarbonyl intermediate undergoes a rapid loss of the coordinating CO molecule at room temperature. Finally, the dianionic intermediate reacts with a new molecule CO_2 restarting the electrocatalytic cycle.

Keywords: Carbon dioxide, Ruthenium, Electrocatalyst, CO_2 reduction, Computational studies

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1. Introduction

In the last decades, the concentration of carbon dioxide in the Earth's atmosphere has been significantly increased because of burning fossil fuels including coal, petroleum fractions, and natural gas (CH_4) to generate energy supply. Today most (>85%) of the energy used worldwide is produced from fossil fuels [1]. As a consequence, the concentration of carbon dioxide has increased in the atmosphere and reached a record high of almost 31.6 billion tons in 2012 [2]. Owing to the increasing CO_2 emissions, human life and the ecological environment have been affected by global warming and climate changes due to the “greenhouse effect”. Hence, it is extremely important to reduce the level of CO_2 generated and released into the environment in order to minimize the threat of global warming.

While numerous strategies are being developed for CO_2 capture, there is an increasing interest in direct use of carbon dioxide as a C_1 carbon source [3-6]. However, the conversion of CO_2 requires a large amount of energy because CO_2 has the most oxidized state of carbon. Also,

CO₂ is a very stable molecule and resistant to reduction at room temperature [7]. Recently, several methods including chemical, photochemical, electrochemical, and photoelectrochemical reduction of CO₂ have been reported [8–13]. These methods can be beneficial to balancing the carbon cycle and are also of interest as potential components in a carbon-based energy cycle, *i.e.*, $\text{CO}_2 + \text{energy} \rightarrow \text{fuel} \rightarrow \text{CO}_2 + \text{energy}$.

Among the various transformations of CO₂, electrochemical reduction has drawn much attention from both researchers and industries for the past three decades [13-18]. The main problem related to the reduction of CO₂ is its high electrochemical stability. Thus, the electrochemical CO₂ reduction proceeds only at high cathodic overpotential (overvoltage), *i.e.*, at potentials significantly more negative than the Nernst potential. This large overpotential is related to the initial reduction of the CO₂ molecule into the CO₂^{•-} radical-anion [3]. A proper electrocatalyst can facilitate a two-electron or proton coupled multi-electron reaction which requires a lower potential than the single-electron reaction as can be seen in Table 1 [19].

Transition metal complexes are promising candidates as electrocatalysts because their reduction is associated with the appearance of a vacant coordination site which is able to bind CO₂ and thus activate its reduction in the metal coordination sphere [20]. Numerous metal complexes have been used as electrocatalysts for reduction of CO₂ [13,18,21,22] and they can be conveniently divided into three main groups: I) macrocyclic, II) phosphine, and III) polypyridyl complexes [23]. The first examples were reported by Meyer and co-workers in 1988 [24], who demonstrated that Rh and Ir polypyridyl complexes are capable electrocatalysts for the CO₂ reduction in DMF under air-free and ambient conditions. Since then, efforts were made to speed up the studies on both the electrocatalytic and photocatalytic CO₂ reduction by different groups

including Meyer [25–31], Fujita [32–36], Kubiak [13,37], Saveant [38] Abruna [39–42], Bocarsly [9,43–46], and others [47–50].

It has been found that the direct electrochemical reduction of CO₂ results in a variety of products, the distribution of which critically depends on reaction conditions. In particular, the electrocatalytic reduction of CO₂ to CO has been reported for the polypyridyl complexes of Re(I) [13,51–53], Os(II) [26,54,55], and Ru(II) [27,56–58] in recent years. The production of CO from the electrocatalytic reduction of CO₂ is more thermodynamically and electrochemically favorable than other two-electron reduction products (Table 1). CO itself can be used as a fuel or used as a precursor compound for the fuel synthesis processes, where CO and H₂ are mixed as synthesis gas (syngas) to form hydrocarbons such as methane and olefins or alcohols such as methanol in the Fischer-Tropsch (FT) process [59].

Our group has very recently reported the synthesis, structure, and spectroscopic characterization of the complexes of Ru(II) [60], Re(I) [61,62], Gd(III) [63], and Dy(III) [63] with different ligands including 4,4'-dimethyl-2,2'-bipyridine (dmb), 1,10-phenanthroline-5,6-dione (phen-dione), 2,4,6-tri(pyridine-2-yl)-2H-1,3,5-triazine-1-ide (tptzH⁻), and Alizarin yellow GG (AyGG), demonstrating that they exhibit outstanding performances for electrocatalytic or photocatalytic reduction of CO₂ to CO.

Herein, we report the facile synthesis of a new mononuclear polypyridyl Ru(II) complex, [Ru(tptz)(CH₃CN)Cl₂] (tptz = 2,4,6-tri(2-pyridyl)-1,3,5-triazine). The complex has been characterized by single crystal X-ray crystallography, elemental analysis, electrochemical and spectroscopic methods. Further, the electrocatalytic activity of this complex has been investigated for the reduction of CO₂ to CO by cyclic voltammetry (CV) in the acetonitrile solution. The computational studies were also performed for the electrocatalytic reduction with

density functional theory (DFT) calculations to support the suggested reaction mechanism. The DFT calculations provided detailed mechanistic information in agreement with the experimental observations.

2. Experimental

2.1. General procedures

All reagents and solvents were commercially available and were used as received. CO₂ with a purity of $\geq 99.8\%$ was purchased from Sigma-Aldrich Company. Elemental analyses were performed using a Leco CHNS-932 elemental analyzer. FT-IR spectra were recorded in the 4000–400 cm⁻¹ region as KBr pellets on an FT-IR JASCO 680-PLUS spectrophotometer. Electronic absorption spectra were recorded on a JASCO 7580 UV-vis-NIR double-beam spectrophotometer using quartz cells with a path length of 10 mm. All voltammetric experiments were performed on a SAMA Research Analyzer M-500. The electrolytic cell consisted of a double-walled glass crucible with an inner volume of ≈ 10 mL which was fitted with a Teflon lid incorporating a three-electrode system consisting of a Pt disk working electrode, a Pt wire auxiliary electrode and a Ag wire as a pseudo-reference electrode (the potential values reported *vs.* SCE). The Pt disk working electrode surface was manually cleaned with 1- μ m diamond polish prior to each scan and rinsed with doubly distilled water between each polishing step. Cyclic voltammetry (CV) of an acetonitrile solution of [Ru(tpz)(CH₃CN)Cl₂] was carried out with a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Acetonitrile was dried over P₂O₅ and vacuum distilled. Ferrocene ($E^\circ = +0.38$ V *vs.* SCE in acetonitrile at 25°C) was used as an internal reference at the end of each experiment [64]. The solutions were purged with N₂ or CO₂ streams during the CV studies. Before injection to the electrochemical cell, the CO₂ or N₂ flow was passed through a silica-gel drier (trap) to remove

any humidity. All spectral and electrochemical data were collected at ambient temperature except where noted. Gas chromatograms were recorded with a Varian STAR 3400 gas chromatograph with helium as the carrier gas at a flow rate of 36 mL/min and a temperature of 235°C.

2.2. Synthesis of $[Ru(tptz)(CH_3CN)Cl_2] \cdot CH_3CN \cdot 0.68H_2O$

$RuCl_3 \cdot xH_2O$ (0.10 g, 0.38 mmol) and tptz (0.12 g, 0.38 mmol) were dissolved in 15 mL of absolute ethanol, and the dark purple mixture was refluxed for 4 h. After cooling overnight, a dark purple precipitate was obtained. It was collected by filtration, washed with cold ethanol (3×10 mL), and then dried under vacuum. The yield of $[Ru(tptz)Cl_3]$ was 89% (0.177 g). *Anal. Calc.* for $C_{18}H_{12}Cl_3N_6Ru$ (519.75 g/mol): C, 41.59; H, 2.31; N, 16.16. Found: C, 41.51; H, 2.27; N, 16.05%.

$[Ru(tptz)Cl_3]$ (0.160 g, 0.30 mmol) was dissolved in a mixture of acetonitrile/ethanol (5:2 v/v), and followed by the addition of $AgNO_3$ (0.05 g, 0.30 mmol). The dark purple mixture was then refluxed in the dark under an N_2 atmosphere for one hour. After cooling overnight, the purple solution was filtered through Celite to remove the fine $AgCl$ precipitate and the filtrate was evaporated to dryness using a rotary evaporator. Purification of the crude product, $[Ru(tptz)(CH_3CN)Cl_2]$, was carried out on an alumina column (grade III, WA, 30×1 cm column). Elution with acetonitrile/toluene (1:1 v/v) gave a dark purple band of the pure complex ($[Ru(tptz)(CH_3CN)Cl_2]$), which was collected, evaporated to dryness, and then recrystallized by diffusion of diethylether into an acetonitrile solution of the complex. After one week at room temperature, single crystals of $[Ru(tptz)(CH_3CN)Cl_2] \cdot CH_3CN \cdot 0.68H_2O$ suitable for X-ray crystallography were formed in a yield of 64% (0.11 g). *Anal. Calc.* for $C_{22}H_{19.4}Cl_2N_8O_{0.68}Ru$ (584.39 g/mol): C, 45.66; H, 3.47; N, 19.36. Found: C, 45.38; H, 3.51; N, 18.97%. UV-vis

(CH₃CN): $\lambda_{\text{max}} = 546$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1} = 13080$); 385 (11800); 284 (40280); 254 (28033); 202 (45130) nm. IR (KBr pellet): $\nu = 1343, 1400, 1468, 1535, 1563, 1658$ (C=C) and (C=N); 1958 (C $\equiv$ N) cm^{-1} .

2.3. X-ray crystallographic analysis

A dark violet single crystal with dimensions of $0.5 \times 0.3 \times 0.2$ mm was chosen for the single-crystal X-ray diffraction study. Data were collected on a Bruker-AXS APEXII four-circle diffractometer equipped with a CCD camera using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 100(2) K under a stream of flowing nitrogen. Structure solution (direct methods) and refinement (full-matrix least-squares against F^2 in anisotropic approximation for all non-hydrogen atoms) were carried out using the SHELXTL program package [65]. Absorption effects were corrected with the semi-empirical multi-scan approach using SADABS [66]. Hydrogen atoms were positioned geometrically (C–H = 0.93; 0.97 Å) and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms. The water molecule of crystallization is partly occupied (occupancy 0.68); its H atoms could not be located by Fourier difference methods and thus were not included in the final model. Details of the data-collection and refinement parameters are given in Table 2. Selected bond lengths and angles are listed in Table 3. Crystal data of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2] \cdot \text{CH}_3\text{CN} \cdot 0.68\text{H}_2\text{O}$ have been deposited at the Cambridge Crystallographic Data Center (CCDC No. 1446155).

2.4. Computational details

All calculations were carried out using the GAUSSIAN 09 computational package [67]. The structure of each species involved in the proposed electrocatalytic cycle was fully optimized without any symmetry restrictions using density functional theory (DFT) at the B3PW91 [68,69] functional and an SDDall [70,71] basis set for all atoms in both the gas and solution phases. The

polarized continuum model (PCM) [72,73] was used for modeling the solvent to optimize the structures in acetonitrile as the solvent. Further, the energies of the frontier molecular orbitals (FMOs) were determined at the same level of theory.

3. Results and discussion

3.1. Synthesis

At first, $[\text{Ru}(\text{tpz})\text{Cl}_3]$ was synthesized *via* reaction of tptz with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in ethanol. The elemental analysis of the product, $[\text{Ru}(\text{tpz})\text{Cl}_3]$, was entirely consistent with its proposed composition. Then, the reaction of $[\text{Ru}(\text{tpz})\text{Cl}_3]$ in refluxing acetonitrile/ethanol mixture in the presence of AgNO_3 under an N_2 atmosphere yielded a new mononuclear Ru(II) complex, $[\text{Ru}(\text{tpz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (Scheme 1). The CHN analysis data of crystallized $[\text{Ru}(\text{tpz})(\text{CH}_3\text{CN})\text{Cl}_2] \cdot \text{CH}_3\text{CN} \cdot 0.68\text{H}_2\text{O}$ are entirely consistent with its composition as determined by single-crystal X-ray crystallography. The complex appears stable in solution for days and no evidence of decomposition was seen in the solid state. The complex has good solubility in common polar organic solvents such as acetonitrile.

3.2. Description of the structure of $[\text{Ru}(\text{tpz})(\text{CH}_3\text{CN})\text{Cl}_2] \cdot \text{CH}_3\text{CN} \cdot 0.68\text{H}_2\text{O}$

X-ray quality crystals of $[\text{Ru}(\text{tpz})(\text{CH}_3\text{CN})\text{Cl}_2] \cdot \text{CH}_3\text{CN} \cdot 0.68\text{H}_2\text{O}$ were obtained by diffusion of diethylether into a concentrated acetonitrile solution of the complex at room temperature. The molecular structure of the complex molecule with a partial atom numbering is shown in Fig. 1. The Ru(II) atom is surrounded by two chloride anions in a *trans* configuration, the κ^3 -tpz ligand chelates through three N atoms, and the acetonitrile CH_3CN molecule coordinates via the N atom. The Ru(II) atom exhibits an overall distorted octahedral $\text{Cl}_2\text{N}_3\text{N}'$ coordination environment, with the tptz ligand arranged in a meridional fashion through one

triazine N and two adjacent pyridyl N atoms, adopting a terpyridyl-like (tpy-like) coordination mode [74,75] with five-membered chelate rings. The Ru–N bond lengths are in a normal range whereby the Ru–N_{triazine} bond (1.917(3) Å) is significantly shorter than the two Ru–N_{pyridyl} bonds (2.066(3) and 2.076(3) Å) (Table 3). This motif is observed in numerous other metal complexes with this type of tpy-like ligands [75,76], due to the stronger π -accepting properties of the triazine ring and/or due to the constricted coordination geometry imposed by the triazine ligand [74,77]. As expected, the Ru–Cl bond lengths of 2.3897(9) and 2.3959(10) Å are significantly larger than the Ru–N distances.

The ideal bite angles for a tridentate ligand in an octahedral environment would be 90 and 180°. However, the bite angles of the coordinating tptz ligand are less than the ideal angles with 78.90(11), 79.60(12) and 158.49(11)°, respectively. These bite angles are comparable to those reported previously for Ru–tptz complexes and are typical of those found with other five-membered chelate ring systems [75,78]. The distortion from an ideal octahedral geometry is also revealed by the difference in the range of *cisoid* [78.90(11)–103.16(11)°] and *transoid* angles [158.49(11)–177.68(12)°]. It has been proposed that the reason of the octahedral distortion is primarily caused by an interior bending of the coordinating pyridyl rings in the tptz ligand and the constraints forced by the five-membered chelate rings. This is reflected in the bite angles involving the coordinating N_{triazine} atom and the adjacent N_{pyridyl} atoms. The tptz ligand is moderately planar, with a rms deviation of 0.054 Å from the least-squares plane through the 24 non-hydrogen atoms (highest deviation 0.119 Å for C19 being part of the pendant pyridine ring). The dihedral angles between the planes of the triazine ring (N2/C6/N3/C7/N4/C8) and the adjacent coordinating pyridyl rings (N1/C1–C5) and N5/C9–C13) are 3.50(19) and 1.93(17)°, respectively, whereas the angle is 4.1(2)° for the pendant pyridyl ring (N6/C14–C18). The two

coordinating pyridyl rings are nearly coplanar with a dihedral angle of $3.56(19)^\circ$. In the crystal structure, one CH_3CN and one partly occupied H_2O solvent molecule are present per complex molecule. Although the H atoms of the water molecule could not be determined during the present study, $\text{O}\cdots\text{N}$ contacts of $2.92\text{ \AA}$ to one of the non-coordinating $\text{N}_{\text{pyridyl}}$ atoms (N6) and of $3.09\text{ \AA}$ to the one of the free $\text{N}_{\text{triazine}}$ atoms (N4) as well as an $\text{O}\cdots\text{Cl1}$ contact of $3.07\text{ \AA}$, point to typical hydrogen bonding interactions important for sustaining the crystal cohesion. Besides additional weak non-classical $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\text{Cl}$ and $\text{C-H}\cdots\text{N}$ interactions also involving the solvent acetonitrile molecule, slipped π - π interactions between the triazine ring and one of the pyridine rings of a neighboring complex (shortest centroid-to-centroid distance $3.73\text{ \AA}$) might consolidate the crystal packing.

3.3. IR and UV-vis spectroscopic studies

The FT-IR spectrum of the free tptz ligand exhibits three strong bands at 1651 , 1572 and 1521 cm^{-1} that are related to $\nu(\text{C}=\text{N})$ vibration of the triazine ring, and $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ vibrations of the pyridyl rings, respectively [77,79]. Another intense band at 1370 cm^{-1} is assigned to the ring stretching vibrations of both the triazine and pyridine rings of tptz. The FT-IR spectrum of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ shows an absorption pattern in the $4000\text{--}400\text{ cm}^{-1}$ region similar to that observed for the tptz ligand. The intense absorption bands that appear around $1343\text{--}1658\text{ cm}^{-1}$ are ascribable to the $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, and ring stretching vibrations of the pyridyl and triazine rings for the coordinated tptz ligand. As compared to the free tptz ligand, these bands exhibit both shifts and splitting, which indicate complex formation and the involvement of triazine and pyridyl nitrogens in coordination to Ru(II) . Further, another

predominant vibration for this complex is associated with $\nu(\text{C}\equiv\text{N})$ at 1958 cm^{-1} that demonstrates the existence of a coordinating CH_3CN molecule.

The electronic spectral data for the Ru(II) complex were measured in CH_3CN solution and data have been presented in the experimental section. The complex exhibits three intense absorption bands in the UV region, at 202, 254, and 284 nm, due to the ligand-centered $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the coordinating tptz chromophore, which are only somewhat perturbed by the complexation in comparison with those of the free tptz ligand [75,77,80]. Also, it shows two lower-energy broad absorption bands in the visible region around 385 and 546 nm, which are both assigned to the $d_\pi (t_{2g}^6 \text{ of Ru}^{\text{II}}) \rightarrow \pi^*(\text{tptz})$ metal-to-ligand charge transfer (MLCT) transitions. Such multiple MLCTs have been observed in several Ru(II) complexes and may result from the splitting of the $d_\pi (t_{2g}^6)$ orbitals of Ru(II) and thus lowering the symmetry from regular octahedral (O_h) [81,82].

3.4. Electrochemical properties of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ under an N_2 atmosphere

To study the electrochemical properties of the complex, cyclic voltammetry experiments were carried out on a CH_3CN solution of the complex (1 mM) with 0.1 M TBAH as the supporting electrolyte under an N_2 atmosphere at room temperature. The cyclic voltammogram of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ at a Pt disk working electrode is shown in Fig. 2, which shows four reduction couples at 1.66, -0.86 , -1.10 , and -1.50 V vs. SCE. The electrochemical reactions associated with these reduction couples are given as follows:

The formal potential ($E_{1/2}$) was determined from the average of the anodic and cathodic peak potentials, where $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ at a scan rate of 0.1 V s^{-1} . The Ru(III/II) couple exhibits equivalent anodic and cathodic current waves, the peak separation ($\Delta E = 0.66 \text{ V}$) of which is independent of the scan rate ($0.1\text{--}0.5 \text{ V s}^{-1}$). The three quasi-reversible reduction waves at negative potentials are assigned to the sequential reductions of the tptz ligand [77,83]. The peak currents for the Ru(III/II) couple change linearly with the square-root of scan rates ($v^{1/2}$) from $0.1\text{--}0.5 \text{ V s}^{-1}$, revealing that this electrochemical step is diffusion-controlled.

3.5. Electrocatalytic activity of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ on the CO_2 reduction

The electrocatalytic activity of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ toward the CO_2 reduction was investigated using simply bubbling CO_2 through a CH_3CN (1 mM) solution by cyclic voltammetry. In order to compare the behavior of the complex under two different atmospheres (N_2 or CO_2), the experiments were studied under the same experimental conditions. The cyclic voltammograms of the complex (1 mM in 0.1 M TBAH/ CH_3CN at a Pt working electrode) purged with an N_2 or CO_2 stream for ~ 15 min from -0.5 to -2.0 V (which is related to the tptz-based reductions) are shown in Fig. 3. As can be seen, there are significant changes in the voltammograms when N_2 is replaced by CO_2 . In the electrocatalyst solution saturated with CO_2 , the second reduction wave is approximately unchanged compared to the N_2 -saturated solution, while the third reduction wave is replaced by two new reduction waves at $E_{\text{pc}} = -1.41$ and -1.80 V . These results are comparable to those reported for similar complexes [27,60,84].

The observed current at $E_{\text{pc}} = -1.80 \text{ V}$ is related to the electrocatalytic CO_2 reduction according to the following reactions:

The proposed mechanism for the CO_2 reduction in the presence of the electrocatalyst, $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$, in acetonitrile is shown in Scheme 2. The initial reduction at the polypyridyl ligands, which act as the electron reservoirs for subsequent CO_2 reduction at the metal atom, is important for electrocatalytic activity of their complexes [27,60,84]. As shown in Scheme 2, $[\text{Ru}^{\text{II}}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ undergoes two sequential one-electron tptz-based reductions to yield $[\text{Ru}^{\text{II}}(\text{tptz}^{2-\cdot})(\text{CH}_3\text{CN})\text{Cl}_2]^{2-}$ followed by rate-limiting substitution of CO_2 for CH_3CN , **eqn (II)** [27,60,84]. In this reaction, an intramolecular two-electron transfer occurs from the $\text{tptz}^{2-\cdot}$ diradical dianion to the coordinating CO_2 ligand to yield the metallocarboxylate intermediate, $[\text{Ru}^{\text{II}}(\text{tptz})(\text{CO}_2^{2-})\text{Cl}_2]^{2-}$, which facilitates the reduction of CO_2 . Tanaka *et al.* [85] found an evidence for a related protonated metallocarboxylic acid intermediate by addition of OH^- to solution of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{2+}$. The similar metallocarboxylate intermediates have been characterized by Meyer *et al.* for $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{Mebim-py})(\text{S})]^{2+}$ (Mebim-py = 3-methyl-1-pyridylbenzimidazol-2-ylidene) through the electrocatalytic reduction of CO_2 to CO in CH_3CN [27,84]. This proposed intramolecular two-electron transfer is also well supported by theoretical calculations (see section 3.6). The metallocarboxylate intermediate undergoes further two consecutive tptz-based one-electron reductions, **eqn (III)** and **(IV)**. In the next step, an oxide transfer occurs from $\text{Ru}^{\text{II}}(\eta^1\text{-CO}_2^{2-})$ to the second CO_2 molecule to yield

$[\text{Ru}^{\text{II}}(\text{tptz}^{2-\bullet})(\text{CO})\text{Cl}_2]^{2-}$ and CO_3^{2-} as the products, **eqn (V)** [27,60,84]. The produced CO_3^{2-} anion is very stable at room temperature in CH_3CN and cannot convert back to the free CO_2 . The characterization of the produced carbonate plays a key role to support the proposed electrocatalytic mechanism. The produced carbonate ions was easily precipitate in the presence of an aqueous solution of calcium or barium ions as calcium or barium carbonate. In addition, the formation of the carbonate anion was confirmed by ^{13}C NMR ($\delta \approx 163\text{--}170$ ppm) and IR spectroscopy ($\nu_{\text{CO}} \approx 1438\text{--}1441$ cm^{-1}).

In the final step, the doubly reduced CO intermediate, $[\text{Ru}^{\text{II}}(\text{tptz}^{2-\bullet})(\text{CO})\text{Cl}_2]^{2-}$, undergoes CH_3CN substitution to release a CO molecule at room temperature and a mono(acetonitrile) intermediate, $[\text{Ru}^{\text{II}}(\text{tptz}^{2-\bullet})(\text{CH}_3\text{CN})\text{Cl}_2]^{2-}$, is formed, **eqn (VI)**. The characterization of the formed CO plays another key role to support the proposed electrocatalytic mechanism. The formed CO was confirmed by both GC and IR spectroscopy (gas phase, $\nu_{\text{CO}} = 2121$ and 2170 cm^{-1}) after electrolysis of the reaction mixture (electrocatalyst in the TBAH/ CH_3CN solution saturated with CO_2) for 5 h at room temperature.

To confirm the catalytic activity of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ and to determine its selectivity for the CO_2 reduction, the controlled potential electrolysis (CPE) was used. After the electrolysis of a solution containing the Ru(II) complex in 0.1 M TBAH/ CH_3CN saturated with CO_2 at a controlled potential of -1.80 V for 5 h, the gas sample was taken using a gas-tight syringe and the production of CO was detected by GC and IR. No detectable quantity of CO gas was found in the headspace of the blank solution (0.1 M TBAH/ CH_3CN saturated with CO_2 in the absence of the Ru(II) catalyst) after electrolysis at -1.80 V for 5 h at 25°C . There is a quantitative Faradic efficiency for the production of CO without generation of H_2 and/or formate ion during the electrolysis time (5 h) for the solution of the complex saturated with CO_2 . Therefore, the

Faradaic efficiency for H₂ and/or formate production is 0%. The analysis of CO produced during the electrolysis experiments by GC at different times reveals that the amount of CO (μmol) is directly proportional to the number of electrons consumed during the electrocatalytic process. In addition, the Faradaic efficiency for the formation of 16 μmol of CO gas over a 5 h electrolysis period at -1.80 V was found to be $> 92\%$. The turnover number for the formation of CO is ≈ 8 (Fig. S1).

The cyclic voltammetry studies of the electrocatalyst solutions after each electrolysis run for a period of 5 h show that the Ru(II) complex is stable during the electrocatalytic reaction. In addition, the UV-vis spectra of a CH₃CN solution of the complex before and after the electrolysis process were completely same, which confirm the stability of the complex during the electrocatalytic reaction (Fig. S2). Fig. 4 shows that the cyclic voltammograms of the electrocatalyst are stable under the CO₂ atmosphere after 10 continuous scans.

The voltammograms of the electrocatalyst under a CO₂ atmosphere at scan rates of $0.1\text{--}0.5\text{ V s}^{-1}$ are shown in Fig. 5. The current value for the wave at $E_{\text{pc}} = -1.80\text{ V}$ (forth wave in Fig. 3), which corresponds to the electrocatalytic CO₂ reduction, varies linearly with the square-root of the scan rate ($v^{1/2}$) (Fig. 6), which confirms a diffusion-controlled mechanism. Fig. 7 shows the cyclic voltammograms of the electrocatalyst solution saturated with CO₂ at different concentrations at room temperature. The reduction peak current increases with increasing concentration of the electrocatalyst from 0.5 to 2 mM. As shown in the inset of Fig. 7, the variation of i_{cat} versus $[\text{cat}]$, $[\text{cat}]$ = concentration of the Ru(II) catalyst, is linear which consistent with the expression in the Randles-Sevcik equation (eqn 1):

$$i_{\text{cat}} = n_{\text{cat}}FA[\text{cat}](D_{\text{cat}}k_{\text{cat}})^{1/2} \quad (1)$$

Where, $[cat]$ is the concentration of the Ru(II) complex in mol L^{-1} , $n_{\text{cat}} = 2$ is the electrochemical stoichiometry for the reduction of CO_2 to CO, $F = 96485.3 \text{ C mol}^{-1}$ is the Faraday constant, A is the surface area of the working electrode (Pt disk) in cm^2 , D_{cat} is the catalyst diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$, and k_{cat} is the rate constant of the electrocatalytic reaction [86].

Eqn (2) is a common application of Randles–Sevcik formula, where, i_d is the diffusion current at $E_{\text{pc}} = -1.10 \text{ V}$ under N_2 which is relatively unchanged in the presence of CO_2 , R is the gas constant, T is the temperature in K, v is the scan rate, and $n = 1$ is the number of the electrons involved in the electrocatalytic reaction [86]. Fig. S3 shows the plot of i_{cat}/i_d versus $v^{-1/2}$.

$$i_{\text{cat}}/i_d = 2.242(k_{\text{cat}}RTn_{\text{cat}}^2/n^3Fv)^{1/2} \quad (2)$$

The effect of the CO_2 purging time on the activity of the electrocatalyst was also investigated at room temperature (Fig. 8). As can be seen, the reduction peak current increases steadily as the CO_2 purging time increases from 5 to 30 min. It is obvious that the concentration of dissolved CO_2 in the electrocatalyst solution is controlled by varying the purging time and has a positive effect on the electrocatalytic activity, so that a larger current is obtained for longer CO_2 purging time because more dissolved CO_2 molecules are available for the electroreduction. The cyclic voltammograms of the electrocatalyst under a CO_2 atmosphere in different temperatures are shown in Fig. 9. The cyclic voltammograms of the Ru(II) electrocatalyst under a CO_2 atmosphere in different temperatures are shown in Fig. 9. As can be seen, the electrocatalytic activity of $[\text{Ru}(\text{tpz})(\text{CH}_3\text{CN})\text{Cl}_2]$ is decreased at lower temperatures, because the solubility of CO_2 in the solution inversely changes with the temperatures. Thus, a decrease in the reaction temperature leads to an increase in the solubility of CO_2 and provides more CO_2 molecules in their solvated forms. Nevertheless, the lower temperatures increase the free energy barrier of the overall reduction reaction and decrease the reaction rate, because activation energy

(E_a) is temperature-dependent. Fig. 9 shows that, however, the solubility of CO₂ is significantly increased at low temperature, the free energy barrier of the overall reduction reaction increases. Consequently, the electrocatalytic activity is decreased at lower temperatures due to a decrease in the reaction rate.

3.6. Theoretical calculations

The computational study was performed to investigate the geometries and electronic structures of the complexes and intermediates involved in the proposed electrocatalytic cycle (Scheme 2). Fig. 10 shows the optimized structure of [Ru(tptz)(CH₃CN)Cl₂] along with the selected bond lengths and angles, which is comparable to its solid-state structure (Fig. 1). Moreover, the optimized structures of the species involved in the proposed electrocatalytic cycle in both the gas and solution phases are shown in Schemes 3 and 4, respectively.

The 3-D plots of the frontier molecular orbitals (FMOs) of the complexes and intermediates involved in the electrocatalytic cycle with their energy levels in both the gas and solution (CH₃CN) phases are shown in Figs. 11 and 12, respectively. The HOMOs and LUMOs of these species have mostly both character of the *d*-orbitals of Ru(II) and π^* orbitals of the coordinating tptz ligand. The HOMO of the initial electrocatalyst, [Ru(tptz)(CH₃CN)Cl₂], is localized on the Ru(II) and Cl[−] moieties and has a mixed metal/ligand character. Similar to many polypyridyl Ru(II) complexes [60,82], the LUMO of [Ru(tptz)(CH₃CN)Cl₂] has a molecular orbital that is mainly localized on the tptz ligand with π^* in both phases. As shown in Scheme 2, the first step (**Ia** and **Ib**) of the proposed electrocatalytic mechanism involves two sequential one-electron tptz-based reductions. The first one-electron reduction of the electrocatalyst, [Ru(tptz)(CH₃CN)Cl₂], yields **Int1** in which an electron enters the empty LUMO. This orbital

has π^* -character of the coordinated tptz ligand. Then, **Int1** performs the second one-electron reduction and the electron is located at the LUMO of **Int1** which has again π^* -character of tptz. Therefore, the two frontier electrons are mainly localized on the coordinating tptz ligand in $[\text{Ru}^{\text{II}}(\text{tptz}^{2-\bullet})(\text{CH}_3\text{CN})\text{Cl}_2]^{2-}$ (**Int2**). The first step is followed by the substitution of CO_2 for CH_3CN (**step II**) and resulted in the formation of **Int3** as a metallocarboxylate intermediate ($\text{Ru}^{\text{II}}(\eta^1\text{-CO}_2^{2-})$) with the C–O bond lengths being 1.264 and 1.286 Å in the gas phase, and 1.275 and 1.303 Å in solution. The optimized structure of **Int3** (Schemes 3 and 4) demonstrates that the CO_2 molecule coordinates to the $\text{Ru}(\text{II})$ ion as a C–bonded ligand which has lower energy than the O–bonded (Ru-OCO) isomer. Upon the coordination of CO_2 to $\text{Ru}(\text{II})$ and formation of **Int3** in both the gas and solution phases, the geometry of CO_2 changes from a linear shape to a bent shape with an increase in the C–O bond lengths. Further, the coordination of CO_2 to the $\text{Ru}(\text{II})$ ion leads to the formation of the CO_2 -character molecular orbitals which can be better electron acceptors than those of the free CO_2 molecule [60]. The DFT calculations confirm the suggested internal two-electron transfer from the coordinated $\text{tptz}^{2-\bullet}$ diradical dianion to the coordinated CO_2 ligand to yield **Int3**, $[\text{Ru}^{\text{II}}(\text{tptz})(\text{CO}_2^{2-})\text{Cl}_2]^{2-}$, which subsequently undergoes further two consecutive one-electron tptz-based reductions, **steps III** and **IV**. Figs. 11 and 12 show that the HOMO and LUMO of **Int3** and **Int4** are primarily localized on the tptz ligand, so, the next two external electrons enter the tptz-character molecular orbitals. The next step (**step IV**) is followed by the abstraction of an oxygen atom from the coordinating CO_2 ligand (**Int5**) by the free CO_2 molecule to yield CO_3^{2-} and a $\text{Ru}(\text{II})\text{-CO}$ intermediate, $[\text{Ru}^{\text{II}}(\text{tptz}^{2-\bullet})(\text{CO})\text{Cl}_2]^{2-}$ (**Int6**). Finally, to complete the cycle, **Int6** releases a CO molecule and converts to a CH_3CN -coordinating intermediate (**Int2**).

4. Conclusions

In this work, a new mononuclear Ru(II) complex, $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$, based on the tridentate ligand tptz has been synthesized and structurally characterized indicating a distorted octahedral environment around Ru(II). This complex showed an efficient electrocatalytic activity for the reduction of CO_2 to CO in CH_3CN . The DFT calculations indicate that the reaction proceeds in six steps initiating by two sequential one-electron reductions at the tptz ligands. The reductions are followed by substitution of CO_2 for CH_3CN which is associated with an intramolecular two-electron transfer from the $\text{tptz}^{2\bullet}$ diradical dianion to the coordinating CO_2 ligand to form a metallocarboxylate intermediate. The adduct of CO_2 to Ru(II) results in an increase in the carbon–oxygen bond lengths while the geometry of the coordinating CO_2 ligand changes from a linear to a bent shape. The next step occurs through an O^{2-} transfer from the coordinating- CO_2 ligand to the free dissolved CO_2 to yield CO_3^{2-} and a $\text{Ru}^{\text{II}}\text{--CO}$ intermediate. Therefore, the proposed electrocatalytic cycle needs two CO_2 molecules, which convert to a CO molecule and a carbonate anion. Finally, the electrocatalytic cycle starts again through a rapid loss of a CO molecule from the $\text{Ru}^{\text{II}}\text{--CO}$ intermediate to generate a $\text{Ru}^{\text{II}}\text{--CH}_3\text{CN}$ intermediate. Since the increase of carbon dioxide in the atmosphere is considered as a major contributor to global warming and the climate changes, the conversion of CO_2 to CO as a fuel ($\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2 + \text{energy}$) is an important solution for recycling of carbon and decreasing greenhouse gas emissions.

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Scheme 1. Synthesis route to $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$.

Scheme 2. Proposed reaction mechanism for the electrocatalytic reduction of CO₂ in the presence of [Ru(tptz)(CH₃CN)Cl₂] as the electrocatalyst in CH₃CN.

Scheme 3. The optimized structures of the species involved in the proposed electrocatalytic cycle in the gas phase.

Scheme 4. The optimized structures of the species involved in the proposed electrocatalytic cycle in the solution phase.

Table 1CO₂ reduction potential vs. SHE [19].

Reaction	E° (V)
$\text{CO}_2 + \bar{e} \rightarrow \text{CO}_2^{\bar{\cdot}}$	-1.9
$\text{CO}_2 + 2\text{H}^+ + 2\bar{e} \rightarrow \text{HCO}_2\text{H}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\bar{e} \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$2\text{CO}_2 + 2\text{H}^+ + 2\bar{e} \rightarrow \text{H}_2\text{C}_2\text{O}_4$	-0.49
$\text{CO}_2 + 4\text{H}^+ + 4\bar{e} \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
$\text{CO}_2 + 6\text{H}^+ + 6\bar{e} \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\bar{e} \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$\text{CO}_2 + 4\text{H}^+ + 4\bar{e} \rightarrow \text{C} + 2\text{H}_2\text{O}$	-0.20

Table 2Crystallographic data and structure refinement for [Ru(tptz)(CH₃CN)Cl₂] $\cdot$ CH₃CN $\cdot$ 0.68H₂O.

Chemical formula	C ₂₂ H _{19.4} Cl ₂ N ₈ O _{0.68} Ru
Formula weight	584.39
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.3179(15)
<i>b</i> (Å)	10.7478(16)
<i>c</i> (Å)	12.4182(19)
α (°)	89.308(4)
β (°)	69.476(4)
γ (°)	87.609(4)
<i>V</i> (Å ³)	1163.7(3)
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	0.935
<i>D</i> _x (Mg/m ³)	1.647
Crystal size (mm)	0.5 $\times$ 0.3 $\times$ 0.2
<i>F</i> (000)	579
θ range (°)	1.75 – 30.00
Range of <i>h</i> , <i>k</i> , <i>l</i>	–13/13, –15/15, –17/17
Reflections collected	47590 [<i>R</i> _(int) = 0.041]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6700 / 0 / 310
Goodness-of-fit on <i>F</i> ²	1.172
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0483, <i>wR</i> ₂ = 0.0978
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1113

Table 3Selected bond lengths (Å) and bond angles (°) for [Ru(tpz)(CH₃CN)Cl₂] $\cdot$ CH₃CN $\cdot$ 0.68H₂O.

Ru1–N2	1.917(3)
Ru1–N7	2.065(3)
Ru1–N1	2.066(3)
Ru1–N5	2.076(3)
Ru1–Cl2	2.3897(9)
Ru1–Cl1	2.3959(10)
N1–C1	1.343(4)
N1–C5	1.373(4)
N2–C6	1.348(4)
N2–C8	1.345(4)
N5–C9	1.376(4)
N5–C13	1.336(4)
N7–C19	1.135(5)
N1–Ru1–N2	79.60(12)
N2–Ru1–N5	78.90(11)
N1–Ru1–N7	98.35(11)
N5–Ru1–N7	103.16(11)
N1–Ru1–N5	158.49(11)
N2–Ru1–N7	177.68(12)
Cl1–Ru1–Cl2	177.48(3)

Fig. 1. The molecular structure of the [Ru(tpz)(CH₃CN)Cl₂] complex. Displacements ellipsoids are drawn at the 40% probability level; solvent molecules have been omitted for clarity.

Fig. 2. Cyclic voltammogram of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/ CH_3CN under an N_2 atmosphere at a scan rate of 0.1 V s^{-1} in room temperature (Inset: the Ru(III/II) couple at different scan rates of 0.1–0.5 V s^{-1}).

Fig. 3. Cyclic voltammograms of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/ CH_3CN under an N_2 (purple line) and a CO_2 (green line) atmosphere at a scan rate of 0.1 V s^{-1} in room temperature. The blank solution (TBAH/ CH_3CN without the complex) reveals no reduction current under a CO_2 atmosphere (blue line).

Fig. 4. Successive cyclic voltammograms (10 cycles) of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/ CH_3CN under the CO_2 atmosphere at a scan rate of 0.1 V s^{-1} .

Fig. 5. Cyclic voltammograms of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/CH₃CN under a CO₂ atmosphere at different scan rates of 0.1–0.5 V s⁻¹ in room temperature.

Fig. 6. Plot of the reduction peak current (i_{pc}) at $E_{pc} = -1.80$ V vs. the square-root of the scan rates ($v^{1/2}$).

Fig. 7. Cyclic voltammograms of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ in 0.1 M TBAH/ CH_3CN under a CO_2 atmosphere at different concentrations of the complex at a scan rate of 0.1 V s^{-1} in room temperature. The inset shows the plot of the reduction peak current (i_{cat}) at $E_{\text{pc}} = -1.80 \text{ V}$ vs. $[\text{cat}]$, the concentration of the Ru(II) catalyst.

Fig. 8. Cyclic voltammograms of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/CH₃CN under a CO₂ atmosphere at different purging times of CO₂ at a scan rate of 0.1 V s⁻¹ in room temperature.

Fig. 9. Cyclic voltammograms of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ (1 mM) in 0.1 M TBAH/ CH_3CN under a CO_2 atmosphere at different temperatures at a scan rate of 0.1 V s^{-1} .

Fig. 10. The optimized structure of $[\text{Ru}(\text{tptz})(\text{CH}_3\text{CN})\text{Cl}_2]$ in the gas phase (the hydrogen atoms are omitted for clarity). The selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$): $\text{Ru}(1)\text{--Cl}(2)$, 2.440; $\text{Ru}(1)\text{--Cl}(3)$, 2.440; $\text{Ru}(1)\text{--N}(4)$, 2.027; $\text{Ru}(1)\text{--N}(31)$, 2.069; $\text{Ru}(1)\text{--N}(32)$, 1.914; $\text{Ru}(1)\text{--N}(33)$, 2.072; $\text{N}(32)\text{--Ru}(1)\text{--N}(33)$, 79.071; $\text{N}(31)\text{--Ru}(1)\text{--N}(32)$, 78.970; $\text{N}(4)\text{--Ru}(1)\text{--N}(33)$, 100.927; $\text{N}(4)\text{--Ru}(1)\text{--N}(31)$, 101.031; $\text{N}(31)\text{--Ru}(1)\text{--N}(33)$, 158.042; $\text{N}(4)\text{--Ru}(1)\text{--N}(32)$, 179.990; $\text{Cl}(2)\text{--Ru}(1)\text{--Cl}(3)$, 175.422.

Fig. 11. Schematic representation of the calculated FMOs of the species involved in the proposed electrocatalytic cycle with their energy levels (eV) in the gas phase.

Fig. 12. Schematic representation of the calculated FMOs of the species involved in the proposed electrocatalytic cycle with their energy levels (eV) in solution (CH_3CN).