Indian Journal of Chemistry
Vol. 60A, March 2021, pp. 356-360

1D and 2D Cobalt(II) coordination polymers with dipicolinic acid ligands and photocatalytic CO_2 reduction

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Received 12 May 2020; revised and accepted 03 December 2020

1D and 2D cobalt(II) coordination polymers, $[Co(2,3\text{-dpc})(H_2O)_2]_n$ (**1**), $[Co(2,5\text{-dpc})(H_2O)_3]_n$ (**2**) and $[Co(3,5\text{-dpc})(H_2O)_2]_n$ (**3**) (dpc = dipicolinic acid dianion) have been successfully synthesized by reaction of dipicolinic acid ligands with CoF_2 in aqueous methanolic solution under hydrothermal conditions. High resolution mass spectroscopy investigation reveals the forming process of CO during the photocatalytic CO_2 reduction and the plausible mechanisms are proposed.

Keywords: Dipicolinic acid, Cobalt(II) coordination polymers, Photocatalytic CO_2 reduction

Decreasing the CO_2 levels and converting it to valuable products are highly desired today[1-5]. Since the reactions involving CO_2 require a significant energy import and always accompany the injection of electrons and protons, thus, research on improvement of catalyst efficiency has gained high attention[6–10]. Among the reported catalysts, homogeneous molecular catalysts of metal complexes have advantages on its freedom of selective arrangement between metals and ligands, enabling us to design superior catalysts for efficient CO_2 reduction[11]. In early reports, molecular catalysts with Ru-and Re-carbonyl cores and ligands based on 2,2′-bipyridine (bpy) have been investigated extensively for their photocatalytic performance[12-17]. However, the cost of Ru and Re precludes their utilization on a large scale. Nowadays, earth-abundant, first-row transition metal catalysts rather than the precious metals are more attractive for an economically viable, sustainable development[18-20]. Recently, molecular catalysts based on first-row transition metals including Mn[21-23], Fe[24,25], Co[26-28] and Ni[29-32] have been studied for photocatalytic CO_2 reduction.

Among different multidentate species, dipicolinic acid (dpc, 2,3-dpc,2,5-dpc or 3,5-dpc) are widely studied ligands for producing stable transition metal coordination polymers and supramolecular architectures[33,34]. The ligands have versatile ligating abilities with transition metals. They can form polymeric or dimeric complexes by carboxylate bridges between metal centers. They can also form tridentate (O, N, O') chelation to one metal ion in simple or mixed ligand complexation.

Herein, we reported three 1D and 2D Co(II) coordination polymers with dipicolinic acid ligands as the homogeneous molecular catalysts for visible-light-driven photocatalytic reduction of CO_2 to CO in the photocatalytic system using **[Ru]** ($Ru(bpy)_3Cl_2$) as a photosensitizer, BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole) as an electron donor, TEOA (triethanolamine) as a CO_2 absorberand a light-emitting diode (LED) blue light (18 modules, centered at 460 nm) as light source. Furthermore, the plausible mechanisms for the photocatalytic reduction of CO_2 to CO were proposed.

Materials and Methods

All reagents and solvents were commercially available and used without further purification. Cyclic voltammetry (CV) was performed using a Model CHI600 instrument (CH Instruments) in a three electrode cell with a pure nitrogen (N_2) and CO_2gases. A three-electrode system was adopted: a glassy-carbon as working electrode (3 mm diameter), an $Ag/AgNO_3$ (0.01 M, 6 mm diameter) as reference electrode and a Pt (1×10 mm) as counter electrode. Scan rate is always 0.1 $V\cdot s^{-1}$.The photocatalytic reduction of CO_2 to CO was conducted under 1 atm of CO_2 at room temperature. The reaction mixture have a total volume of 6 mL, containing catalyst, [Ru], BIH, and DMF/TEOA (v/v= 5:1). Before irradiation, the solution was bubbled with N_2 for 10 min and CO_2 for 30 min. The reaction mixture was continuously stirred with a magnetic bar and irradiated under the blue

LED light. The generated gases were analysed by a gas chromatography (GC-2014C, TDX01 molecular sieve, column (3 m × 2 mm), INJ 50 °C, TCD 100 °C, column temperature 50 ℃, carrier gas flow 30 mL/min). The amounts of products were determined using the external standard method as the basis for quantitative analysis. Calibration curves for H_2, CO were established separately. The number of moles of H_2 and CO in the sample headspace were determined by converting peak integrations from GC data into moles by using individual calibration curves and taking into account of the irradiated sample volume. Complexes [Co(2,3-dpc) (H2O)2]n (**1**)[35], [Co(2,5-dpc)(H2O)3]n (**2**)[36] and [Co(3,5-dpc)(H2O)2]n **(3)**[37] were synthesized in a modified procedure according to the previous literature reported. The detailed synthesis procedure of complexes **1**, **2** and **3** are structural characterizations are given in Supplementary Data (Figs S1-S6).The single crystal structures complexes **1**, **2** and **3** are given in Fig. 1, respectively.

Results and Discussion

In the typical photocatalytic reaction, a DMF/TEOA (5:1, v/v) mixed solution (6 mL) containing cobalt complex (2 mg) and BIH (20 mg) was irradiated using 450 nm LED blue light (12 W), giving CO as the main product with H_2. Moreover, no HCOOH was found in the detection of the liquid phase by ion chromatography[38] (Supplementary Data, Figs S7a, 7b and 7c). As is shown in Fig. 2, the turnover number (TON) based on the Co-complex **1** reached 5.08 (0.39 μmol) after 5 h irradiation, 6.144 (0.44 μmol) for complex **2** and 7.207 (0.55 μmol) for complex **3** after 7 h irradiation. The experimental result showed that complex **3** has a better catalytic efficiency than complex **1** and complex **2**. To confirm the effect of photosensitizer on catalytic performance, by using eight different photosensitizers (20 mg, [Ru], FI, CNA, Anthraquione, Rhodamine B, Erythrosine

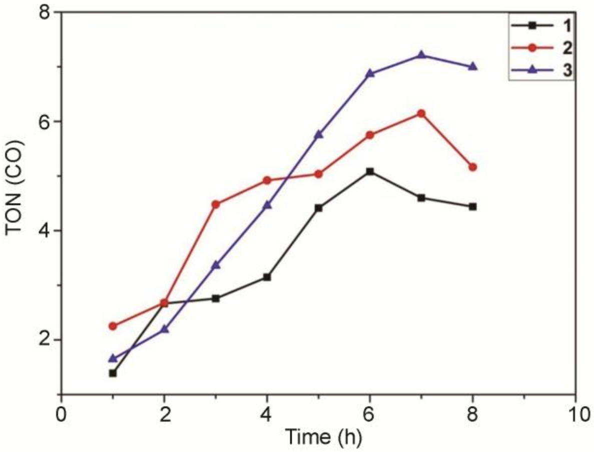


Fig. 2 — Photocatalytic conversion of CO_2 to CO by complex **1** (black), **2** (red) and **3** (blue), (CO_2 reduction was carried out in 6 mL CO_2-saturated CH_3CN/H_2O/TEOA (3:2:1 v/v) solution with 2 mg catalyst, 2 mg [Ru], 20 mg BIH and irradiated with the blue light of 460 nm)

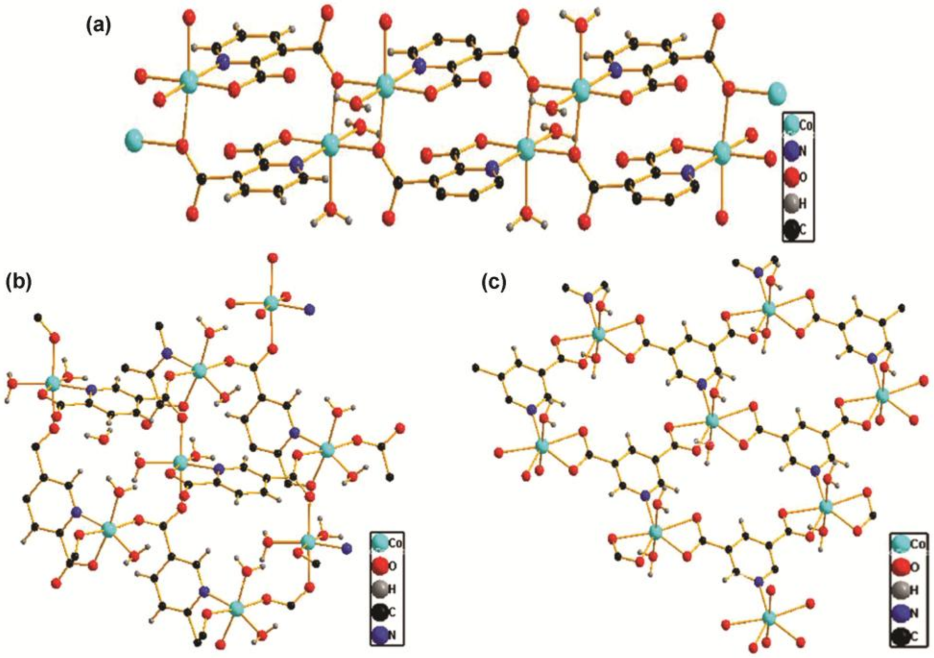


Fig. 1 — Structure of a fragment of complex (a) **1,** (b) **2** and (c) **3**

B, Eosine B, Purourin), we found that [Ru] showed the best catalytic effect as a photosensitizer (Supplementary Data, Fig. S8).As CO and H_2 are two-electron-reduced products of CO_2 and protons, respectively, and BIH is also a two electron donor, accordingly, BIH is used as a sacrificial agent during the irradiation. The number of incident photons to the sample was 2.01×10^{24} photons per hour by using the classical iron ferrioxalate ($K_3Fe(C_2O_4)_3$) chemical actinometer. According to the quantum yield calculations[39] and using known parameters[40], the quantum yield of CO formation are Φ_{co} = 0.0000117 (for complex **1**), 0.0000132 (for complex **2**), 0.0000165 (for complex **3**).

CV measurements were performed to investigate the electro-chemical behaviours of the complexes **1**, **2** and **3** in DMF/TEOA (v/v=5/1) under $N_2$and CO_2 atmospheres. As shown in Fig. 3, an irreversible one-electron reduction wave of Co complex **3** was observed at $E_{1/2}$ = -1.52 V vs $Ag/AgNO_3$ at 100 mV s^{-1}, which is assigned as $Co^{II/I}$ reduction, which is positive than the two reduction waves of complex **1** and complex **2** ($E_{1/2}$ = -1.53, and -1.55 V, respectively, in Supplementary Data, Figs S9 and S10). The results are in accordance with the previous report[41]. When CO_2 is introduced, the intensity of the current peak increased, exhibiting that these three complexes are active electrocatalysts for CO_2 reduction. Moreover, the reduction peaks of the three complexes were more positive than the redox potential of **[Ru]** ($E_{1/2}$ = −1.75 and −1.91 V), indicating that the visible light driven CO_2 reductive reaction is thermodynamically feasible with the three complexes as catalysts and **[Ru]** as a photosensitizer.

High-resolution mass spectrometry (HRMS) was used to detect the active intermediates under a given catalytic conditions (Fig. 4 and Supplementary Data, Figs S11 and S12). During the process of photocatalytic reaction, the intermediates $Ru(bpy)_3^+$and the transition product of **1**, **2** and **3** were detected by HRMS. Fig. 6 clearly showed peaks at m/z values of 569.1031 and 285.0555,

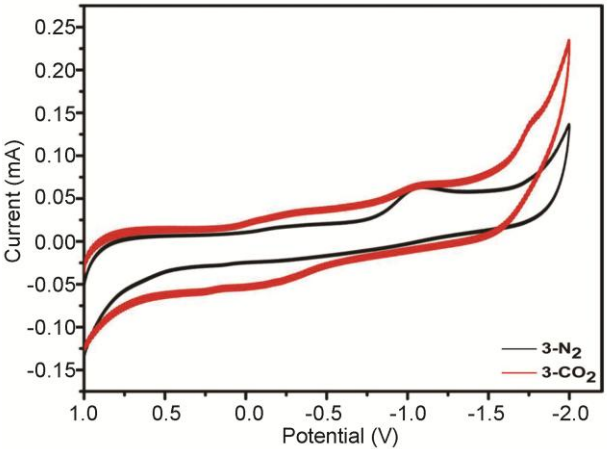


Fig. 3 — CV plot of CO_2 reduction in 0.1 M of $^nBu_4PF_6$ and 20 mg complex **3** in a solution of DMF/TEOA (v/v=5/1), scan rate=100 mV/s, with a glassy carbon as working electrode, Pt wire as counter electrode, and an $Ag/AgNO_3$ (0.1 M $AgNO_3$) as reference electrode

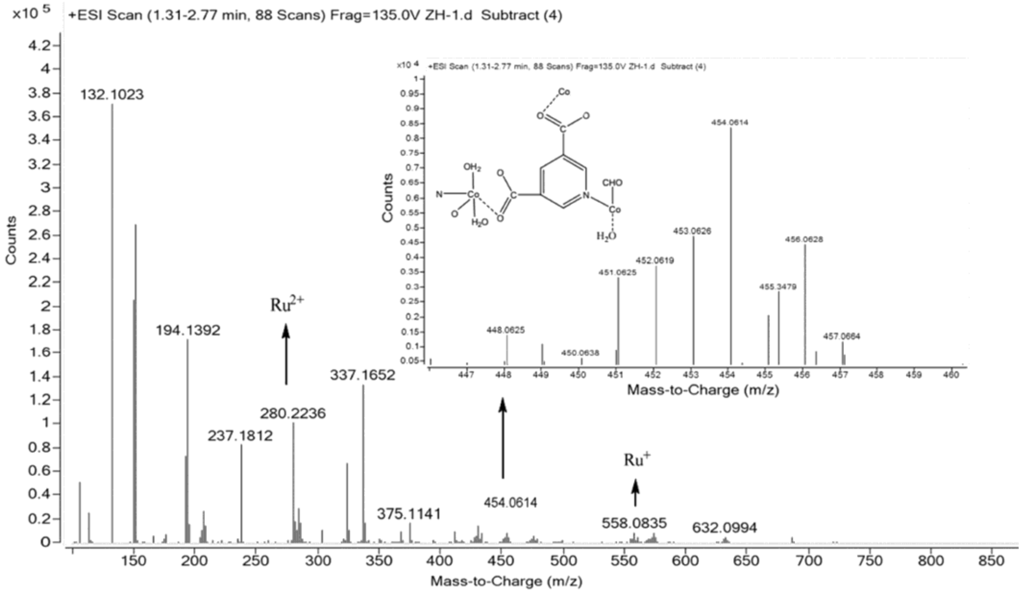
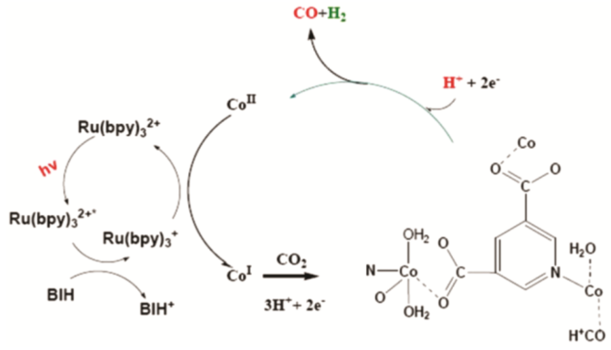


Fig. 4 — HRMS spectra of CO_2-saturated DMF/TEOA solution (v/v, 5:1) containing 0.077 mM compound **3**, 0.45 mM [Ru] and 0.178 mM BIH after irradiation for 3 h



Scheme 1 — Proposed mechanism for the photocatalytic reduction of CO_2 to CO for complex **3** / [Ru] /BIH/TEOA system

attributed to $\mathbf{[Ru]^+}$and $\mathbf{[Ru]^{2+}}$, respectively. The signal at m/z = 454.0614 was ascribed to the $[R\text{-}Co^I\text{-}HCO\text{-}H_2O]^+(R=Co_2N(3,5\text{-dpc})(H_2O)_2$ (N=pyridyl N atom of the ligand) adduct generated by **3**. Therefore, based on the results of catalytic experiments presented as well as previous reports on photocatalytic CO_2 reduction, a mechanism based on PCET (proton-coupled electron transfer) was deduced[42] (Scheme 1): the catalytic process starts from photoexcitation of the photosensitizer ($Ru(bpy)_3^{2+}$) to form an excited state photosensitizer ($Ru(bpy)_3^{+}$) *via* light irradiation and the excited electron is subsequently transferred to the catalyst by a sacrificial agent BIH. Then the complex **3** is reduced by $Ru(bpy)_3^{+}$ through oxidative quenching to form a Co(I) species, then Co(I) species binds with a CO_2 molecule which is subsequently protonated to form a $[Co^I\text{-}HCO\text{-}H_2O]^+$adduct, which is different from the $[Co^I\text{-}CO_2\text{-}H]^+$ adduct generated by **1** and **2** (in Supplementary Data, Scheme S1 and S2). The catalysts were regenerated with the release of CO and H_2. The intermediate of **3** is more favourable to the production of CO, which could explain the higher catalytic efficiency of **3** compared to that of **1** and **2**. For complex **3,** one cycle of catalysis needed 4 electrons and 4 protons in the whole, while for complexes **1** and **2**, 2 electrons and 2 protons are needed for their catalytic cycles (in Supplementary Data, Scheme S1 and S2).

Conclusions

In summary, we have reported three homogeneous molecular catalysts of the cobalt(II) coordination polymers with the dipicolinic acid ligands (2,3-dpc, 2,5-dpc or 3,5-dpc) for visible-light-driven photocatalytic reduction of CO_2 to CO. Further investigation revealed that CO formation was observed during the photocatalytic CO_2 reduction process and the mechanisms based on PCET were proposed.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(03)356-360_SupplData.pdf.

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China (No.21661034).

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