

Cobalt Complexes As Homogeneous Electrocatalysts For CO₂ Reduction: An Experimental And Computational Study

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Carbon dioxide (CO₂) is known to be one of the largest contributors among greenhouse gases to the well-known problem of global warming. On the other hand, CO₂ can also be considered as one of the most abundant and accessible carbon sources. Indeed, under appropriate conditions, it could be used as a cheap, fossil-free building block for the preparation of more complex derivatives and intermediates. Among the different approaches for its conversion, electrochemistry represents one of the most promising methods because it is a straightforward, clean and very versatile technique. Nevertheless, CO₂ conversion by electrochemical methods is highly limited by kinetics; thus, the use of appropriate catalysts to lower the overpotential and control the mechanistic pathways is necessary.

In this context, electrocatalysts based on metal complexes have proved to be a good option. In fact, through variation of the metal center or a rational ligand design, they can be modified to fit specific purposes, such as improve solubility or stability, promote specific inter-molecular interactions or enhance and tune spectroscopic or electrochemical properties. Among the many metal complexes proposed as electrocatalysts for CO₂ reduction, those bearing non-innocent ligands receive significant attention: indeed, the localized electron density on the ligand portion of the complex in its reduced state allows the ligand to interact with CO₂ via σ and π bonds.

For these reasons, four cyclopentadienyl-phenylenediamino-cobalt complexes **I-IV** bearing different substituents at the phenylene moiety (figure 1) have been studied as catalysts for the CO₂ reduction [1]. Moreover, the effect induced by the replacement of one of the two amino groups of the phenylenediamine ligand with a sulfur atom was investigated synthesizing the corresponding complex with 2-aminobenzenthioate **V** [2]. In the latter case, the replacement of a nitrogen donor with a bigger and more polarizable sulfur atom should enhance the efficiency of the complex in stabilizing the extra charges and the catalyst-CO₂ adduct, due to the presence of *d*-orbitals in the first coordination sphere.

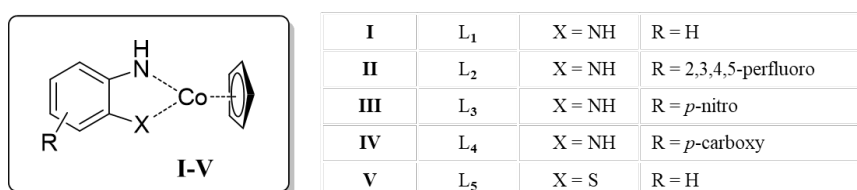


Figure 1 – Molecular structures of complexes **I-V**.

These compounds were characterized by cyclic voltammetry measurements in DMSO both under nitrogen and CO₂ atmospheres, showing an increase in the cathodic current ranging from 3.36 (**III**) to 5.59 times (**II**) that of the measurement under nitrogen (figure 2a). Moreover, with the addition of water, the current enhancement in the presence of CO₂ reaches 31.07 times in the case of complex **II** (figure 2b). Regarding the presence of sulfur atom, complex **V** showed the higher current enhancement in the presence of CO₂ (9.41) under anhydrous conditions, while the effect of water is reduced by the lack of the second amino group. Interestingly, these complexes exhibit very good selectivity toward CO₂ reduction with respect to hydrogen evolution even in the presence of water.

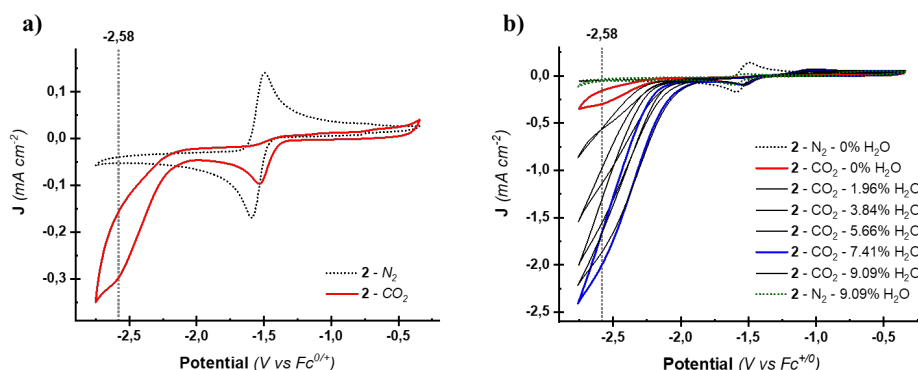


Figure 2 – a) Cyclic voltammeteries of complex **II** under N_2 atmosphere and in saturated CO_2 solution. Panel a) refers to anhydrous conditions, panel b) shows to the effect of the presence of water.

In addition, these results were analyzed and rationalized by means of density functional theory (DFT) calculations and Fukui functions analysis employing the B3LYP functional and using the 6-311+G(d,p) basis set for all atoms, taking into the account the solvent effects using the polarizable conductor-like continuum model (CPCM) for the DMSO solvent. In particular, DFT results clearly show the effects of different substituents on the electrochemical properties of these compounds: in fact, calculation of HOMO and LUMO (figure 3a) well agrees with the experimental results. Moreover, the Fukui functions analysis (figure 3b) indicates that the most favorable positions for an electrophilic attack on the reduced complex are the nitrogen and cobalt atoms.

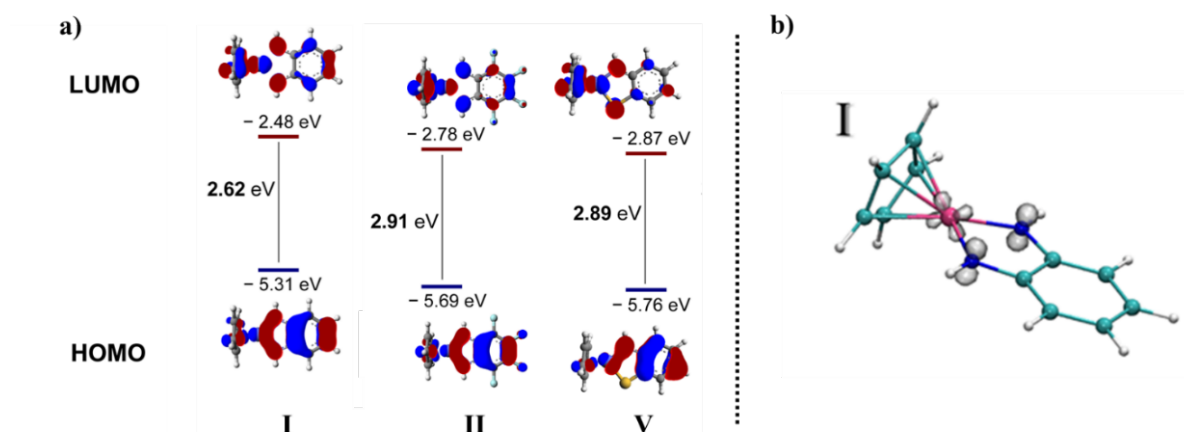


Figure 3 – a) Representative calculated frontier orbitals for complexes **I**, **II** and **V**. b) Fukui function analysis of the monoreduced parent complex **I**, showing the most favorable position for the CO_2 adduct formation.

To sum up, among the tested derivatives, complex **V** showed the higher electrocatalytic activity in the reduction of CO_2 in anhydrous DMSO, with over 9-times current enhancement with respect to the complex under N_2 atmosphere. At the same time, the fluorinated complex **II** proved to be a better choice in DMSO/ H_2O mixture, due to the presence of a second NH coordinating group, which favors catalyst- H_2O interactions.

REFERENCES

- [1] Melis N, Mocci F, Vacca A, Pilia L, (2020) "Novel homogeneous selective electrocatalysts for CO_2 reduction: an electrochemical and computational study of cyclopentadienyl-phenylendiamino-cobalt complexes". *Sustainable Energy Fuels*, 4, 5609-5617. DOI: 10.1039/d0se00790k
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