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Double Bridged µ₂-Halide Cu (II) Complexes for the Electrocatalytic **Reduction of CO₂**

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Abstract:

Two dicopper (II) complexes of general formula [CuLX₂]₂ {L=2, 5-diphenyl-3, 4(2-pyridyl) cyclopenta-2, 4-dien-1-one, X= Cl (1) or Br (2) have been synthesized and characterized by elemental analysis, IR, UV-Vis spectroscopic methods. The crystal structures of both complexes have been determined by single-crystal X-ray diffraction; 1 and 2 have binuclear structures and Cu (II) centers in both complexes adopt a distorted square pyramidal geometry. Two [CuLX] (X=Cl or Br) units in both complexes are linked via μ -X coordination bridge modes with the Cu-Cu distances of 3.534 and 3.716 Å for 1 and 2 respectively. The electrochemical behavior of the free L ligand and the corresponding Cu (II) complexes was studied in acetonitrile. The cyclic voltammetry of the complexes 1 and 2 show three ligand based reduction processes and two metal-centred reductions that are assigned to copper (II) to copper (I) and copper (I) to copper (0). The electrocatalytic activity for the reduction of CO₂ of the two complexes was investigated; both complexes are active for the CO₂ reduction and result in the formation of CO.

Keywords: Binuclear complexes, Copper (II) complexes, Crystal Structure, Electrocatalyst, CO₂ reduction

1- Introduction

The current global energy landscape heavily relies on the burning of fossil fuels including coal, oil and natural gas. Indeed, these sources of energy represent more than 85 percent of the energy used worldwide [1]. Since fossil fuels are non-renewable, concerns about a possible energy crisis caused by a dearth of fossil fuels are growing. Energy extraction from the burning of fossil fuels also results in a foreboding emission of carbon dioxide (CO₂). As this increase in the CO₂ concentration in the atmosphere is linked to global warming and climate changes, there is an urgent need for reducing the accumulation of CO₂ in the atmosphere. Indeed, Solomon et al.'s climate modelling studies have shown that the effect of the latest increase in the CO₂ concentration of the past decades would take up to 1000 years to subside, even if new emission could be prevented. Hence, not only the release of CO₂

into the environment has to cease as soon as possible to minimise the adverse impact of climate changes, but the captured CO_2 should also be turned into valuable fuels [2-4].

Different methods, including radio-, thermo-, photo-, electro- and bio-chemical ones, have been reported for the conversion of CO_2 to other chemicals like CO, formate, methane and methanol [5]. Among them, the electrochemical reduction of CO_2 has drawn much attention because it has several advantages: (1) Electro-chemical conversion can be performed at room temperature and ambient pressure. (2) The supporting electrolytes can be fully recycled so that the overall chemical consumption can be minimized to simply water or wastewater. (3) The electro-chemical reaction systems are compact, modular, on-demand, and easy for scale-up applications. (4) The necessary electricity to drive the process can be obtained, without generating any new CO₂, from solar, wind, hydroelectric, geothermal, tidal, and thermoelectric processes [6]. The reduction of CO₂ is, however, a difficult task because the carbon atom is in its most oxidized state and is thermodynamically stable. Thus, the electro-chemical CO₂ reduction proceeds only at high over-potential. These large overpotentials are related to the initial conversion of the CO_2 molecule into the CO_2 radical anion. Electro-catalysts are therefore primordial for decreasing the over-potentials required for an electrochemical reaction and for opening up routes for energetically less demanding reactions [7]. Amongst the catalysts used for the reduction of CO_2 , metallic catalysts need-large over-potentials for CO_2 reduction and the study of the mechanisms of these systems are usually difficult. Moreover, the electrode surface suffers from poisoning by the intermediates or products of catalysis [8]. Transition metal complexes can serve as molecular catalysts in the reduction of CO₂ at lower over-potentials through undergoing multiple reductions and thus storing multiple redox equivalents in both the ligand and metal ion. Many complexes with different ion centres and various macrocyclic, polypyridyl and phosphine ligands have been used as an CO_2 reduction electro-catalysts [9-11]. Among them, the polypyridyl class of ligands offer many advantages. Indeed, polypyridyl ligands have been shown to be redox active and capable of assisting in mediating multi-electron transformations. Additionally, polypyridyl ligands are ubiquitous archetypes within inorganic complexes and have generally been shown to be stable and synthetically versatile. These ligands afford the ability to precisely control coordination geometries and electronic structures around a desired metal centre [10-12].

In recent years, copper (II) complexes containing pyridyl ligands and amine donors have been studied as electro-catalysts for the reduction of CO₂ [13-22]. Because in these complexes nitrogen donor atoms in the backbones of pyridyl ligands can be bound to CO₂ in the form of carbonate [23-24]. Examples of such compounds are [N, N'-bis(2-R-phenyl-salicylidenaminato)Cu(II)] (R= Me, Cl), [N,N'-bis (salicylaldimine)propylenediimino Cu(II)], [Cu₂(m-xpt)₂(NO₃)₂](PF₆)₂ , [Cu₂(mxpt)₂(Cl)₂](PF₆)₂ (xpt= m-xylylene pyridyltriazole group) [23-24].

We report the synthesis and characterization of a series of new binuclear copper complexes containing the ligand L with bromo and chloro bridging ligands (Scheme 1). We also report the crystal structures as well as the spectroscopic and electrochemical properties of the two Cu (II) complexes. The electrocatalytic activities of these two complexes in the reduction of CO_2 has also been investigated.

2- Experimental

2.1. Materials

All solvents and reagents were obtained commercially and used as received from Aldrich and Merck. Silica gel 60 (70- 230 mesh, Fluka) was used for dehydration. The purity of CO_2 and argon (Ar) was 99.99%, and they were used directly.

2.2. Physical measurements

Elemental analyses were performed on a Perkin–Elmer 2400II CHNS-O elemental Analyzer. UV–Vis spectra were recorded on a double beam Halo DB-20 spectrophotometer. Infrared spectra (KBr pellets) were recorded between 4000 and 400 cm⁻¹ on a Rayleigh WQF-510A FTIR spectrometer spectrophotometer. The electro-chemical measurements were performed on a SAMA 500 Research Analyzer in a three electrodes system consisting of a glassy-carbon-working-electrode, a platinum disk auxiliary electrode and an Ag wire as pseudo-reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 \pm 0.1 mm diameter was manually cleaned with 1 µm

alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte. Acetonitrile was dried over CaH₂. These solutions were deoxygenated by purging them with Ar for 5 min. All electro-chemical potentials were calibrated versus the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal reference under the same conditions [25]. Chronopotentiometry curves were collected out on a Gamry Reference 3000 electrochemical instrument using a homemade air-tight two-chamber cell. Working and reference electrodes were fixed in one chamber and the counter electrode in the other; the two chambers were separated by a frit. Belt-shaped carbon cloths (1071 HCB) with a 1 cm² area exposed to the electrolyte were used as the working electrode. A double-junction protected Ag/AgNO₃ electrode (with acetonitrile containing 1 mM AgNO₃ and 0.5 M TBHP as filling solution) was used as reference electrode, and a platinumwire counter-electrode. The electrolyte in the chamber of the working electrode was vigorously stirred during the experiments. The working electrode side was bubbled with CO_2 for 30 min to get the electrolyte saturated. The inlet gas was pre-humidified by acetonitrile to minimize the evaporation of the electrolyte. Online test of gas-phase products was done on a homemade gas chromatograph (GC) equipped with a Carboxen®-1010 PLOT capillary column and a thermal conductivity detector (VICI) and helium as carrier gas. The flow rate of CO₂ was set to 10 sccm.

2.3. Synthesis

2.3.1. Synthesis of the red ligand (L)

The red ligand 2,5-diphenyl-3,4(2-pyridyl)cyclopenta-2,4-dien-1-one (**L**) was synthesized by thermal dehydration, over silica gel, of its white diol precursor, $LH_2(OH)_2$ according to the method reported in the literature [26].

2.3.2. Synthesis of Cu₂L₂Cl₄ (1)

84.5 mg (0.2 mmol) of the red ligand **L** were added to a solution of CuCl_2 (26 mg, 2mmol) in acetone (15 ml) in an ice bath. The solution was stirred for 15 min at room temperature. Diethyl ether was then allowed to diffuse, at room temperature, slowly into the deep brown solution. The brown crystalline precipitate–was filtered off and dried in vacuum. Crystals of (1) suitable for X-ray

crystallography were obtained by recrystallization from dichloromethane–acetone (10:1 v/v) at room temperature after three days. Yield: 56%. Anal. Calc. for $C_{54}H_{36}$ Cl₄Cu₂N₄O₂: C, 62.26; H, 3.48; N, 5.38. Found: C, 61.64; H, 3.61; N, 6.14%. FT-IR (KBr, cm⁻¹) v_{max} : 1715 (s, C=O), 1585 (m, C=N), 1433 (m, C=C), UV–Vis (acetonitrile): λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹): 514 (300), 297 (3270), 272 (34200).

2.3.3. Synthesis of $Cu_2L_2Br_4$ (2)

The complex **2** was prepared by the same method used for **1**, except that CuBr₂ was used instead of CuCl₂. Recrystallization from dichloromethane gave brownish tabular crystals after one day. The crystals were filtered off, washed with a small amount of cold methanol, and dried under vacuum. Yield: 60%. Anal. Calc. for C₅₄H₃₆ Br₄Cu₂N₄O₂: C, 53.18; H, 2.98; N, 4.59. Found: C, 53.50; H, 3.82; N, 5.04%. FT-IR (KBr, cm⁻¹) υ_{max} : 1715 (s, C=O), 1583 (m, C=N), 1433 (m, C=C), UV–Vis (acetonitrile): λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹): 517 (465), 292 (54171), 270 (58343).



Scheme 1. Synthetic route to $Cu_2L_2X_4$ (X= Cl, Br)

2.4. X-ray crystallography

Suitable tabular single crystals of **1** were recrystallised from dichloromethane/acetone and of **2** from dichloromethane. BRAGG intensities were collected at T= 100 K, using Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å) on a Rigaku SuperNova dual system diffractometer equipped with an Atlas CCD detector. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis*^{Pro} [27].

The solutions and refinements of the structures were performed by the latest available version of

ShelXT [28] and ShelXL [29]. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the "riding" model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its carrier C-atom (1.5 U_{eq} for the methyl groups). Details of the data collection, structure solution and refinement of **1** and **2** are compiled in Table 1 and some geometrical items in Table S1.

The structure **2**, was refined as a two-component inversion twin yielding the value of 0.30(4) for the BASF parameter. In this structure, a solvent mask was calculated with the help of the solvent-masking program in *OLEX2* [30] and 172.0 electrons were found in a volume of 1024.0 Å³ in one void. This is consistent with the presence of one solvent molecule of dichloromethane per formula unit, which accounts for 168.0 electrons.



Fig.1. The structure of the binuclear complex 1. Displacements ellipsoids are drawn at the 50% level. The dimer contains a centre of inversion midway between the copper and the μ^2 -chlorine atoms.

The complex **1** grows in a tabular (100) habit and develops the $\{100\}$ and $\{001\}$ pinacoids and the $\{011\}$ prism. The complex **2** grows in a surprisingly centrosymmetric tabular (001) habit and develops the $\{110\}$ prism and the $\{001\}$ pinacoid unforeseen in this point group.

Table 1. Data collection, structure-solution and refinement for 1 and 2.

Compound	$Cu_2L_2Cl_4(1)$	$Cu_2L_2Br_4.CH_2Cl_2(2)$	
Formula	$C_{54}H_{36}Cl_4Cu_2N_4O_2$	$C_{55}H_{38}Br_4Cu_2N_4O_2Cl_2$	
$D_{calc.}$ / g cm ⁻³	1.495	1.525	
μ/mm^{-1}	3.637	4.844	
Formula Weight	1041.75	1219.59	
Colour	clear light green clear intense brown		
Cryst. Solvents	DCM/ Acetone	DCM/ Acetone DCM	
Habitus	Tabular (100) Tabular (100)		
Size/mm ³	0.23×0.15×0.02	23×0.15×0.02 0.33×0.12×0.01	
<i>T</i> /K	100.0(1)	100.0(1)	
Crystal System	monoclinic	orthorhombic	
Space Group	C2/c	$Pca2_{I}$	
a/Å	22.7229(17)	10.8257(2)	
b/Å	9.7235(7)	25.2316(5)	
$c/\text{\AA}$	22.4497(13)	19.4423(4)	
α /°	90	90	
β/°	111.088(8)	90	
γ/ [°]	90	90	
V/\dot{A}^3	4628.0(6)	5310 66(18)	
Z	4020.0(0)	4	
<u> </u>	05	1	
Wavelength/Å	1.54184	1.54184	
Radiation type		CuKa	
$\hat{\boldsymbol{\mu}}$	4 221	4.444	
$\theta / $	76 448	76 623	
Measured Refl	11573	26911	
Independent Refl	4776	8875	
Reflections with $I > 2(I)$	3474	7892	
$R_{\rm eff}$	0.0406	0.0405	
Parameters	298	595	
Restraints	0	0	
Largest Peak /e Å-3	1 419	1 381	
Deepest Hole / $e Å^{-3}$	-0.849	-0.526	
GooF	1 038	1 037	
wR_2 (all data)	0 1771	0 1057	
wR_2	0.1514	0.1007	
R_1 (all data)	0.0862	0.1000	
R.	0.0595	0.0409	



Fig.2. The structure of the binuclear complex 2. Displacements ellipsoids are drawn at the 50% level.

3- Result and Discussion:

3.1. Synthesis of complexes 1 and 2

Two binuclear complexes containing chloro (1), and bromo (2) halogens in basal (μ_2) and apical positions and the bidentate ligand **L** were prepared in acetone according to Scheme 1. This solvent imposed itself because of its more soluble and stabler complexes compared to those in polar and coordinating solvents such as alcohols, acetonitrile, DMF *etc.*; indeed in the latter strongly solvated species may compete with the formation of the target-complexes. The N–Cu–N bite-angle (84.15(14)° for 1, 86.7(2)° for 2) is a valuable parameter controlled by the linkage between the two pyridine-rings by the CPD-one, but in these structure the free rotation of the pyridyl rings provides some slack (the pyramid only displays symmetry C₁). The kinetic chelate strain effect [31] arising from an increase in the Cu–N bond distance (2.024(5)Å for 1, 2.033(6)Å for 2) and the interaction of the solvent with the copper(II) ions are both involved in the process of formation of the complexes.

3.2. Spectral Studies

The FT-IR spectra of the free red ligand L and its complexes 1 and 2 are shown in ESI (Fig. S1) and full data are presented in section 2.3. The IR spectrum of L exhibits bands between $2860 - 3100 \text{ cm}^{-1}$

which can be attributed to C-H stretching modes of the pyridine rings. Two strong bands at 1715 and 1599 cm⁻¹ correspond to C=O and C=N stretching vibrations and are red-shifted by 5-20 cm⁻¹ [26]. Additional shifts are expected for the ring breathing-mode of **L** occurring at 990 cm⁻¹ and between 1020 - 1025 cm⁻¹ in the IR spectra of the complexes [32, 33].

The electronic absorption spectra of **L** and its metal complexes were recorded in acetonitrile and full data are listed in section 2.3. The intra-ligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of **L** appear at 492 (ε = 1167), 324 (ε = 5021) and 258 nm (ε = 200010). These transitions are slightly red-shifted in the corresponding metal complexes. In the UV-Vis spectrum of **1** (Fig. 3), the peaks in the region of 270-370 nm are assigned to ligand-centred transitions, while the broad absorption bands at 514 nm (ε = 300) and 517 nm (ε = 465) are attributed to d-d transitions in **1** and **2**, respectively, and are in agreement with corresponding ML₅ complexes with C_{4v} symmetry [32-38].



Fig.3. UV-Vis spectra of **1** (a) (700-265 nm, 1×10^{-5} M; 700-350 nm, 1×10^{-4} M) and **2** (b) (700-260 nm, 1×10^{-5} M; 800-350 nm, 1×10^{-4} M) in acetonitrile.

The d-d transition in **1** appears at shorter wavelength than in **2** by ~3 nm, presumably owing to a more efficient overlap between the donor orbitals of the **L** and Cl⁻ ligands with the d-orbitals of the copper (II) centre. This observation is in accord with the shorter Cu–N_{py} (2.032(3) Å) and Cu–Cl_{bridge} (2.4590(8) Å) bonds in **1** as compared to Cu–N_{py} (2.041(3) Å) and Cu–Br_{bridge} (2.6364(6) Å) in **2**. (Table S1).

3.3. Crystal Structures

The crystallographic and refinement data are summarized in Table 1 and selected bond distances, bond and torsion angles are given in Table S1. The molecular structures of **1** and **2** are illustrated in Figs. 1, and 2, respectively; the copper atoms are coordinated by the bidentate red ligand **L** and three halogen atoms.

1 and **2** resemble each other a lot in the solid state (Fig. S2), but are yet different enough so as not to build-up isostructural structures. In particular, **1** crystallises in the monoclinic space group C2/c but **2** in the orthorhombic, non-centrosymmetric, space group Pca2₁. The binuclear complex in **1** displays point symmetry $\bar{1}$ but that in the **2** presents only point symmetry 1. But the two complexes are topologically similar and present close ADDISON-parameters (1500918), too (**1**: 0.22, **2**: 0.17), meaning that they form slightly distorted square pyramids. Each copper of the dimeric unit of a complex is connected to two nitrogen atoms of the pyridine rings from **L**, a chloride ion in the apical position and two chloride ions bridging the Cu(II) centres in the basal plane to form a distorted square pyramidal geometry.

The basal planes in **1** are defined by N1, N2, Cl1 and Cl2 for Cu1 (Fig. 1). The bridging Cu₂Cl₂ moiety is planar with a Cu-Cl1-Cu1¹ angle of 91.75 (4). Also the Cu-Cl bond distances in the bridged Cu₂Cl₂ part are unequal, 2.3389 (12) and 2.579 Å, which are longer than the terminal Cu-Cl₂ bond distance 2.2260 (12) Å. the Cu-Cu distance is 3.543 Å longer than the sum of the two van der Waals radii for copper atom, thus indicating that there is no metal-metal bonding. These values are in good agreement with other dimeric copper chloride compounds [35, 37, 39-41].

The basal planes in **2** are by N1, N2, Br1, Br3 around Cu1 and by N3, N4, Br2 and Br4 for Cu2 (Fig. 2). The Cu-Br bond distances in the Cu₂Br₂ planar bridge are 2.4355 (14) and 2.8359 (12) Å, and the Cu-Br-Cu and Br-Cu-Br bond angles are 89.54 (4) $^{\circ}$ and 90.67 (4) $^{\circ}$, respectively, close to 90 $^{\circ}$, as expected for a square pyramidal geometry around Cu (II) ion. The Cu-Cu distance of 3.716(2) Å, longer than the sum of the two van der Waals radii for copper atoms indicates that there is no metalmetal bonding. These values are in good agreement with similar compounds reported in other papers [35, 38, 41, 42].

The structure of **1** consists of (100) layers. Each half layer is built of dimers the centre of which lie at $(\frac{1}{4}, \frac{1}{4}, 0)$ and of which the long axes point to either [011] or $[01\overline{1}]$. Nearest dimers in a (100) chunk are related by a $\{\sigma_y|00\frac{1}{2}\}$ glide reflection and nearest half layers are related by $\{\sigma_y|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ glide reflection. The structure owes its cohesion to a plethora of weak C-H...Cl hydrogen bonds (Table S2), C-H... π interaction and, of course, van der Waals forces. Note that the lengths of the hydrogen bonds nicely correspond to Steiner's values [43]. All of the weak interactions are intra-molecular (Fig. S3).

The structure of **2** consists of (010) layers in which the long axes of the dimers are all parallel and point, in subsequent blocks, to $[01\bar{1}]$ and [011]. The structure owes its cohesion to a plethora of weak C-H...O and C-H...Br hydrogen bonds (Table S2), C-H... π interactions and, of course, van der Waals forces. Note that the lengths of the hydrogen bonds nicely correspond to Steiner's values [38]. All, but three of the weak interactions are intra-molecular; the inter-molecular ones (parallel to [010]) connect (010) chunks and induce chains along [100] (Fig. S4).

3.4. Electrochemical Studies

The electrochemical properties of the free ligand **L** and its metal complexes **1** and **2** were investigated at 25° C, under an argon atmosphere. Cyclic voltammograms of each compound in 1mM acetonitrile solution were recorded (with 0.1M of TBAH as the supporting electrolyte). Our previous studies [44-46] on the electrochemical properties of ligands containing pyridine residues showed that these ligands were electro-active in the potential range from 0 to -2 V.

The cyclic voltammogram of L (Fig. S5) shows three redox processes at -0.83, -1.32 and -1.54 V that can be assigned to the reduction of the pyridyl rings and lead to the formation of a radical anion [44-46].

Fig. 4 shows a typical cyclic voltammogram of **1** from open circuit potential towards negative values. Three well defined reduction waves at -0.63, -0.81 and -1.63 V and one low current wave at -1.09 V were detected in primary scans. It is not straightforward to assign these cathodic peaks to either metalcentred or ligand-centred processes, but the literature suggests that the two reductions at -0.63 V and -1.09 V are related to $Cu^{II/I}$ and $Cu^{I/O}$ respectively, while the two reduction peaks at -0.81 V and -1.63

V can be attributed to the reduction of the pyridyl rings of coordinated L in 1 [20, 47-49]. More evidence comes from the cyclic voltammograms of 1, measured in different potential ranges. As seen in Fig. 4 by limiting the potential window between 0 - 0.9 V (red curve) the oxidation peak at -0.32 V corresponding to Cu^{0/1} disappears and confirms the statement that the Cu^{1/0} reduction process does not accrues until -0.9 V. The existence of the oxidation peak around -0.06 V was related to the reduction at -0.63V attributed to the Cu^{11/1} couple. By extending the potential window to -1.15 V (green curve), the oxidation peak corresponding to Cu^{0/1} process appears and confirms that the reduction at -1.09 V is due to the Cu^{11/0} couple. The occurrence of a second metal-centred reduction processes (Cu^{1/0}) at negative potentials implies that the species reduced are not stable and that metal ions escape from the complex. These results are supported by the appearance of a very intense oxidative wave at -0.32 V, characteristic of the release of deposited metallic copper from the surface of the electrode.



Fig. 4. Cyclic voltammogram of **1** (**1 mM**) in the potential ranges of (a) 1.25 - 2.2 V (blue curve), (b) 0.02 - 0.95 V (red curve), (c) 0.02 - 1.15 V (green curve) in acetonitrile at 298 K, under an Ar atmosphere and at a scan rate of 0.1 V s⁻¹.

The next oxidation peak at -0.06 V was attributed to $Cu^{I/II}$ and the electrochemically quasi-reversible oxidation process at +0.62 V to the $Cu^{II/III}$ couple, which is consistent with those reported previously [47, 50].



Fig. 5. $Cu^{II/III}$ oxidation process of 1 under an Ar atmosphere at scan rates of $100 - 500 \text{ mV s}^{-1}$.

Fig. 5 reveals a cathodic shift of the Cu^{II/III} oxidation potential with a scan rate increasing from 0.1 to 0.5 Vs^{-1} , and thus confirms the quasi reversible behaviour of the electrochemical reaction. The peak current between 0.10 and 0.50 V s⁻¹ (Fig. 5 inset) depends linearly on the square root of the scan rate; such dependence is typical of a diffusion-controlled current. The number of electrons transferred in a diffusion-controlled process was estimated as two, by using of Bard's equations (see Supplementary Information) [51-52].

The cyclic voltammogram of **2** in acetonitrile (Fig. S6) shows features similar to those observed for **1**. In general, the redox couples of **2** are shifted to more positive values relative to those observed for 1, demonstrating the weaker electron-donation character of Br⁻ in **2** relative to Cl⁻ in **1**. This behaviour confirms the structural data obtained from the X-ray diffraction analysis (Table S1). The average bond lengths of Cu-Cl_{bridge} (2.4590(8) Å) and Cu-N_{py} (2.032(3) Å) in **1** are shorter than Cu-Br_{bridge} (2.6364(6) Å) and Cu-N_{py} (2.041(3) Å) in **2**.

3.5. Study of the activity of 1 and 2 in the Electrocatalytic CO₂ reduction

The electrochemical reduction of carbon dioxide by means of homogeneous electrocatalysts has always been of interest because of its low over-potential compared to that required in the direct reduction on metal electrodes [53]. Since the active redox sites of the polypyridyl ligands are capable of storing multiple redox equivalents, **L** just might play an active role in catalysis [54-55]. The presence of multiple equivalents of electrons in a catalyst can facilitate multi-electron reactivity with CO_2 and evade the energetically costly one-electron reduction of CO_2 to CO_2^{-} . Therefore, the reduced polypyridyl rings just might act as an electron-reservoir in the electrocatalytic reduction of CO_2 in which the metal centre would mediate the transfer of these reducing equivalents to CO_2 , leading to an electrochemical reduction [14].

Once the electrochemical behaviour of **1** and **2** had been studied, the catalytic activity of the latter was also investigated in CO₂ reduction by bubbling CO₂ through an acetonitrile solution of the corresponding complexes and comparing with the results obtained under an argon atmosphere under the same experimental condition. The cyclic voltammograms of **1** in acetonitrile solution in the absence (blue) and in the presence of CO₂ (red) are presented in Fig. 6. The reduction potentials between -0.63 and -1.09 V show no significant changes neither in potential nor in current, while the last ligand-based reduction at -1.63 V is slightly shifted and accompanied by a well pronounced cathodic current peak, corresponding to the CO₂ reduction process (more than 2.3-fold increase in current density with respect to that observed in the absence of CO₂). Moreover, return anodic waves corresponding to the ligand disappeared, too; this indicates that the reduced form of the L is consumed by the reaction with CO₂ [56]. So, we may conclude that a homogeneous electron transfer mechanism in the outer sphere between CO₂ and one of the reduced forms of the complex **1** is responsible for the reduction of CO₂. Additional evidence for this speculation is the appearance of metal-centred Cu^{1/1} oxidations in the voltammogram of **1** in the presence of CO₂.



Fig. 6. Cyclic voltammetry of **1** (1.1 mM) under Ar (blue) or CO₂ (red) in acetonitrile with 0.1 M TBAH supporting electrolyte at 100 mV s.

Complex 2 also shows a 2.8-fold increase in current density of the CO_2 irreversible reduction wave when is saturated with CO_2 in comparison to the saturated complex with Ar (Fig. 7). The other quasireversible reduction waves do not show any significant increase in current density. So, complex 2 can also be used as a moderate electro-catalyst for the reduction of CO_2 (Fig. 7).



Fig. 7. Cyclic voltammogram of 2 (1 mM) in acetonitrile at 298 K, under an Ar (blue) and CO₂ (red) atmosphere and at a scan rate of 0.1 V s⁻¹.

A comparison between the electrocatalytic results of 1 with those obtained for 2 reveals that the presence of the Br⁻ ligand in 2 with a weaker electron-donation character versus Cl⁻ in 1 leads to an increase in the catalytic activity of 2 relative to 1. The complex 2 with bromo ligands therefore seems to perform better in the molecular catalysis of CO₂ [57].

To determine the products of the reduction of CO_2 , long-term chrono-potentiometric electrolysis was performed in 0.5 M acetonitrile solutions of TBHP as electrolyte and 1 mg·mL⁻¹ concentration of catalysts (1 and 2) using a homemade air-tight two-chamber cell (Fig. S7 and Fig. S8). The experimental procedure of measurements was described in section 2.2.

As shown in Fig. 8 and Table 2, CO was the only gaseous product of the electrocatalytic reduction of CO_2 in the presence of the complexes **1** and **2**. Carbon monoxide was not formed, however, when the electrolysis was carried out in the absence of CO_2 ; CO is therefore shown to be produced by the electrocatalytic reduction of CO_2 .

Complex		Fara	Faradic Efficiency (%)		
		СО	HCOO-	H ₂	
1	Without water	10			
	With water	23		47	
2	Without water	25			
	With water	14		52	

Table 2. Faraday efficiencies of different products of **1** and **2** during chronopotentiometry tests at -20 mA·cm⁻² in CO₂ saturated 0.5 M TBHP acetonitrile electrolyte with and without H₂O.

The role of water in the electrochemical reduction of CO_2 by **1** and **2** was investigated by adding a known concentration of H_2O to the electrolyte solution. The reduction of CO_2 in the presence



Fig. 8. GC analysis of a headspace sample of complexes **1** and **2** after 30 min electrolysis experiments in absence and presence of 0.5 M H₂O.

of H_2O yielded CO and H_2 for both complexes (Fig. 8 and Table 2). ¹H-NMR of the electrolyte solution (containing 0.5 M of H_2O and the electro-catalyst) after electrolysis did not reveal any production of formate. As shown in Table 2, the Faradic-yield of CO upon addition of 0.1 M water

increased from 10% to 23% in the gaseous phase for **1**, but decreased from 25% to 14% for **2**. It can be concluded that the presence of Br^- groups, in particular their electron-withdrawing capacity makes electron transfer easier in **2** with respect to **1**.

4- Conclusion

Two binuclear copper (II) complexes of general formula $[CuLX_2]_2$ [X= Cl⁻ (1), Br⁻ (2)] binding the ligand **L** were synthesized and characterized by different spectroscopic methods. X-ray diffraction revealed the two Cu (II) centres to lie in distorted square coordination pyramids, subtended by the monarch-like¹ bidentate ligand **L** and three halide ligands, two of which share an edge in order to form a dimer. The bromo-complex, **2**, incorporates a DCM solvate molecule, hidden behind the wings of the monarch, into its non-centrosymmetric structure. Both complexes owe the cohesion of their layer structures to a plethora of weakest interactions in the solid state. The cyclic voltammetry of both complexes in acetonitrile solution showed three **L**-centred reduction waves and three Cu-based redox processes under Ar-atmosphere. Electrocatalytic studies of **1** and **2** by cyclic voltammetry showed that these complexes can perform an electrochemical reduction of CO₂ to CO with moderate FEs and good stability. The electrocatalytic activity of the bromo bridging-ligands turned out to be superior to that of the chloro ones; this difference is conjectured to be due to an easier electron transfer from the catalyst to CO₂. We shall pursue the flight of the monarch by implementing various other ligands in order to glean more insight into the mechanisms of these redox processes.

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¹ Indeed, the flexible phenyl moieties rather perfectly mimic the wings and movements of a generic butterfly and our favourite is the Monarch.

Supplementary information:

Crystallographic data have been deposited with the CCDC under the following codes: **1** (1862696) and **2** (1862695). Copies of the data can be obtained, free of charge, from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, <u>deposit@ccdc.cam.ac.uk</u> or <u>http://www.ccdc.cam.ac.uk</u>.

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