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Carbon dioxide activation by aza-macrocyclic complexes

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Abstract

Experimental observations of photocatalysis and electroinduced-activation of CO_2 mediated by coordination compounds with aza-macrocyclic ligands are discussed in this review. The production of fuels from the reduction of CO_2 catalyzed by coordination complexes of simple tetraaza-macrocycles, porphyrin, phthalocyanine and biphenanthrolinic hexaazacyclophanes are described. The use of this macrocyclic chemistry, i.e. for simple models, in the development of multipurpose supramolecular functions is emphasized.

Keywords: CO_2; Aza-macrocyclic ligands; Photocatalysis; Electroinduced activation; Reduction

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1. Introduction

The conversion of CO_2 to organic compounds, principally formic acid, for use as fuels and in industrial applications has been studied since the beginning of this century [1,2]. During the last decade, methods of reducing CO_2 to CO, formaldehyde, formate, methanol, methane, oxalate etc., using electrochemical methods which consume less energy, have been developed [3–10]. However, a large-scale method of reducing CO_2, equivalent to photosynthesis in green plants, has not yet been developed. If this is to be achieved, technologies for the removal and reduction of CO_2 will need to become more sophisticated. Since atmospheric CO_2 is one of the gases contributing to the greenhouse effect, and is produced by technologically oriented societies, this aim is of interest in other areas of science [11].

During the last few years many studies of matters such as reduction at metallic electrodes, solvent effects on reaction mechanisms, reduction in the presence of coordination compounds with open and closed macrocyclic ligands, identification and characterization of products and mechanisms, photoelectroactivation and catalytic activity in homogeneous and heterogeneous media, and modified electrodes have been reported [12–18]. The aim of this review is to summarize recent results of investigations of the photo- and electroinduced activation of CO_2 by means of coordination compounds with aza-macrocyclic ligands. A detailed review of these matters appeared some years ago [15]. Additionally, some emphasis will be placed on the use of macrocyclic chemistry in the formation of supramolecular structures.

2. General remarks

General aspects of the physicochemical properties of CO_2 and its reduction at metallic cathodes in different solvents are described in this section.

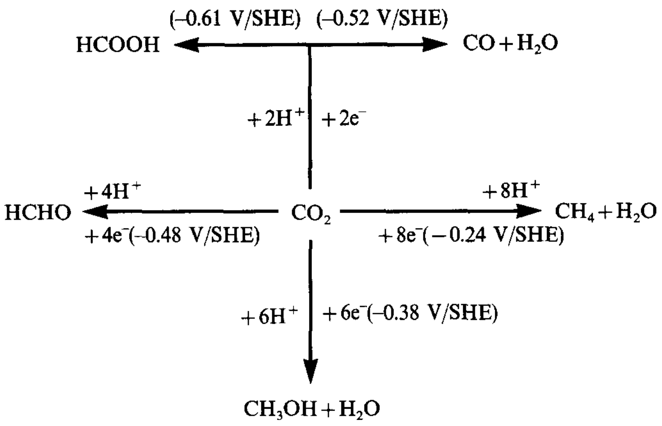
2.1. *Fuels from the reduction of CO_2*

The reduction of CO_2 is an important step in the conversion of this abundant carbon source into organic products. The electrochemical reduction of CO_2 at metal cathodes generally occurs at highly negative potentials, up to −2.24 V vs. SCE [19]. Several reports in the literature have proposed that the transformation of CO_2 into organic compounds can be used as a source of inexpensive fuels and chemicals [12]. Indeed, the reduction of CO_2 could produce formic acid, CO, formaldehyde, methanol or methane in multi-electron transfer reactions as shown in Scheme 1 [19,20].

A comparison of the multi-electron transfer reactions (Scheme 1) with the one-electron reduction of CO_2 to form the $CO_2^{\cdot-}$ anion radical [19,20]

$$CO_2 + e^- \rightleftarrows CO_2^{\cdot-} \qquad \varepsilon^\circ = -1.2\ \mathrm{V} \qquad (1)$$

$$CO_2 + H^+ + e^- \rightleftarrows CO_2H \qquad \varepsilon^\circ = -0.60\ \mathrm{V} \qquad (2)$$



Scheme 1.

shows that the thermochemical advantage of the former reactions (they require less energy than those of Eqs. (1) and (2)) could be balanced by the kinetic constraints imposed by multi-electron transfers. Additional data relating to thermodynamic, reduction and insertion reaction products of the activation have recently been summarized [21].

2.2. Reduction of CO_2 at metallic cathodes

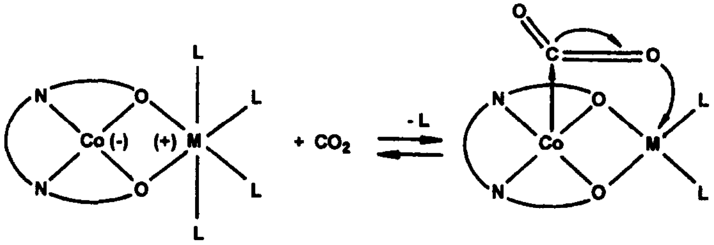
The reduction of CO_2 at metallic cathodes can be driven electrochemically or photochemically [3,22–35]. The aim of these studies was to find cathodes that discriminate against the reduction of H_2O to H_2 and favor the reduction of CO_2. A fundamental requirement is that the latter process occurs at a lower overpotential on such electrodes. Semiconductors have been used as cathodic materials in electrochemical or photoelectrochemical cells [15,36,37]. The low-temperature electrochemical reduction of CO_2 in water to yield CO as the main product has recently been studied [38]. The low-temperature reduction of $KHCO_3$ in aqueous solution takes place at a very low overvoltage on gold electrodes [39]. Moreover, the nature of the products obtained with a copper cathode at room temperature and normal pressure (1 atm) depends strongly on the electrolyte and solvent in cells [26]. When protons are not readily available from the solvent (e.g. *N*,*N*′-dimethylformamide), the electrochemical reduction involves three competing pathways: oxalate association through self-coupling of $CO_2^{\cdot-}$ anion radicals, production of CO via O—C coupling between $CO_2^{\cdot-}$ and CO_2, and formate generation by interaction of $CO_2^{\cdot-}$ with residual or added water [40]. Copper was found to be one of the most effective electrode materials for the generation of hydrocarbons and alcohols from CO_2 reduction [3,23,24]. High efficiencies for hydrocarbon generation were found for short electrolysis times. At longer times, the reaction efficiency decreases with a simultaneous increase in hydrogen evolution and the electrode becomes almost completely inactive [28]. Electrode poisoning has been attributed to the formation of an absorbed intermediate of unknown composition which accelerates hydrogen evolution. It has also been suggested that the loss of catalytic activity depends on the crystallographic properties of the electrode, the surface characteristics and the morphology [28,31,41]. The rate of methanol synthesis from a 1:1 mixture of CO_2 and H_2 at a Cu(100) single crystal has been measured and a kinetic model has been proposed. This model correctly predicts the rates of methanol production in catalysts under industrial conditions. The electrochemical reduction of CO_2 at a copper cathode in methanol gives better yields of methane and insertion products, such as ethylene, than are obtained in water at low temperatures [11].

3. Catalytic CO_2 reduction using coordination compounds

The large overpotential required to drive the electrode reaction at an appropriate rate in the electrochemical reduction of CO_2 at metallic cathodes is an unquestionable technical problem which has been addressed by adding catalysts [15,22,27,42]. The kinetics of these processes can be modified by using catalysts which facilitate multielectron transfers without changing the thermochemical properties of the reactions. A similar strategy can be applied to the photoreduction of CO_2 in homogeneous solutions. Strategies which have been demonstrated experimentally are described below.

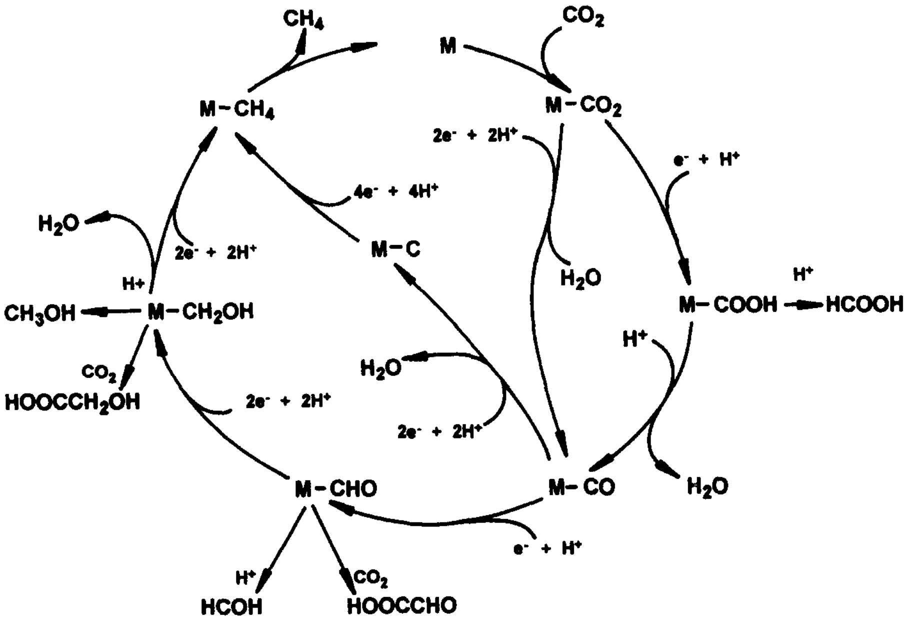
3.1. Coordination compounds with acyclic ligands

Even though the catalytic reduction of CO_2 using coordination compounds with acyclic ligands is not the main subject of this review, some relevant results are presented. The spontaneous fixation of CO_2 by reaction with binuclear complexes of acyclic ligands has been studied in the last decade [16,43–44]. These complexes are bifunctional with nucleophilic and electrophilic sites, a property that allows them to work as reversible carriers:



Spontaneous fixation of CO_2 in air by nickel and Cu(II) complexes via carbonate ligands has recently been reported [45,46]. These new experimental observations have contributed to the development of the mechanisms proposed below.

Transition metal complexes which incorporate polypyridine ligands appear to be particularly active in the electrocatalytic reduction of CO_2 [47–51], as are some transition element complexes of terdentate ligands. In this case, the catalytic process is the result of a subtle balance between stability and reactivity in the reduced form of the complexes, i.e. the form assumed to be reactive.

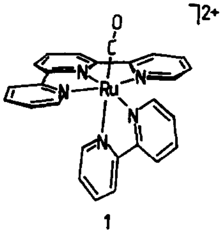


Scheme 2.

Scheme 2 shows a general cycle for the generation of CO_2 reduction products with various complexes of acyclic ligands as electrocatalysts [48–54]. This cycle is also valid for electrocatalysis with macrocyclic ligands (see below).

The electrochemical reduction of CO_2 by $[Ru(bpy)(terpy)(CO)]^{2+}$ (**1**) in ethanol + water at low temperatures produced HOOCCHO and $HOOCCH_2OH$ in addition to CO, HCOOH, HCHO and CH_3OH. The reduction is associated with the stabilization of the Ru—CO bond in $[Ru(bpy)(terpy)(CO)]^{2+}$ (**1**) $[Ru(bpy)(terpy)(CHO)]^{+}$ (**2**) and $[Ru(bpy)(terpy)(CH_2OH)]^{+}$ (**3**) under electrolysis conditions. The competitive addition of protons and CO_2 to these complexes results in products with one carbon atom (HCHO and CH_3OH) and with two carbon atoms (HOCCHO and $HOOCCH_2OH$) [53–56].

Various rhenium, rhodiuim and ruthenium complexes have also been used successfully as catalysts in photochemical and electrochemical processes. These complexes have been used in homogeneous and heterogeneous catalysis [15]. Complexes containing acyclic ligands other than bipyridine derivatives have been used in the electrocatalytic reduction of CO_2 [49,57–67]. These ligands include binary carbonyls [49], phosphines [60,63], alkoxides [57] and hydrides [64]. The reduction products obtained depend strongly on conditions such as solvent, temperature, pH and electrodes. In general, CO and H_2 were the main products, but some with one carbon



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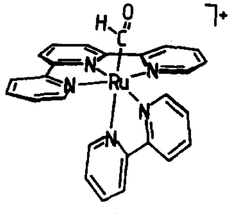

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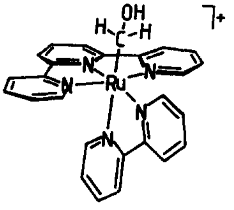

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atom (HCHO, H_2CO, H_3COH and CH_4) and with two carbon atoms were also generated (see Scheme 2).

The electrocatalysis of CO_2 reduction has been carried out in solution and at chemically modified electrodes [68]. Several technical arrangements have been employed successfully [15], of which the use of polymeric complexes immobilized on carbon electrodes [69–71] and the incorporation of complexes into coated Nafion® membranes [72] should be emphasized. Some examples related to the use of macrocyclic systems are reviewed in the following sections.

3.2. Coordination compounds with macrocyclic ligands

Considerable effort has been dedicated to the synthesis and characterization of complexes with macrocyclic ligands. The electrochemical reduction of CO_2 catalyzed by transition metal complexes has been studied extensively during the last decade [12,15,22,56,73–86].

The transition metal complexes investigated included those with polypyridyl ligands [56,77–82] and aza-macrocyclic ligands, such as porphyrins, phthalocyanine [22,73,74,84–86], and various tetraaza-macrocyclic complexes [13,75]. These studies have shown that the chemical properties of these compounds depend on the nature of the ligands. For example, the effect of macrocycles on the spectra and the redox potentials of some Ni(II) complexes has been shown [15]; in addition, the degree of unsaturation and the size of the macrocycle have a pronounced effect on the stability of the oxidation states available to the metallic ion. Thus, in principle, the thermal reactivity of these complexes can be controlled by appropriate structural changes in the ligand [87–91].

Several molecular electrocatalysts have been suggested to diminish the overvoltage; most are based on nitrogen-containing macrocyclic complexes. Thus the indirect electrochemical reduction of CO_2 involves the initial reduction of metal complexes and their subsequent reaction with CO_2. This approach facilitates the reduction of CO_2 at a potential closer to the (reversible) thermodynamic value. Thus the metal complexes are redox-activated catalysts [17].

3.2.1. *Cyclam and cyclam derivative complexes*

The complex of Ni(II) and Co(II) with the macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) (**4**) has been shown to be a particularly effective and selective catalyst for the electrochemical reduction of CO_2 to CO at mercury electrodes in water at potentials much less negative than those required for the uncatalyzed reduction [22,73–75,92]. The ability of $[Ni(cyclam)]^{2+}$ to serve as a catalyst precursor for the electroreduction of CO_2 has prompted many studies of this complex electrochemistry. These previous studies have established the following.

(i) The active catalyst is a form of $[Ni(cyclam)]^{+}$ adsorbed on the surface of mercury electrodes [22,73,75,83,93].

(ii) $[Ni(cyclam)]^{+}$ is adsorbed on mercury over an unusually wide potential range, including potentials that are much more positive than those where $[Ni(cyclam)]^{2+}$ is reduced to unadsorbed $[Ni(cyclam)]^{+}$ [93,94].

(iii) CO is the product of the catalyzed reduction of CO_2 [22,73,83,93,94].

A reasonable explanation for the fact that the adsorbed Ni(I) complex $[Ni(cyclam)]^{+}_{ads}$; but not the same complex in solution, is catalytically active towards the reduction of CO_2 has been provided on the basis of theoretical calculations [95]. The catalytic activity is severely diminished in the presence of CO on unstirred mercury electrodes and, as CO is the primary product of the reduction, this behavior limits the long-term effectiveness of the catalyst. It is proposed that the decrease in activity is due to Ni(cyclam)CO, an insoluble complex of Ni(0), which is formed during the reduction of CO_2. Unfavorable shifts in the potential and decreased catalytic activity were observed when carbon rather than mercury was used as a working electrode with $[Ni(cyclam)]^{2+}$ as the catalyst. This electrochemical behavior is shown in cyclic voltammograms (Fig. 1) for various Ni(II) complexes [75]. Mechanisms for the electrochemical processes at mercury electrodes in solutions of $[Ni(cyclam)]^{2+}$ and CO_2 have been proposed [15,93] (Scheme 3).

Scheme 3 shows the formation of a carbon-bonded Ni(II) complex by reaction of CO_2 with $[Ni(cyclam)]^{+}$. The formation of such a complex is considered to be a fundamental step in the mechanism of the $Ni(cyclam)^{2+}$-catalyzed electrochemical reaction [15]. The overall process for the transformation of CO_2 into CO also involves inner-sphere reorganization. Scheme 3 includes the formation of a sparingly soluble complex containing Ni(0), cyclam and CO which is a product of the reduction of $[Ni(cyclam)]^{2+}$ under CO. Deposition of a precipitate of the Ni(0) complex on the mercury electrodes inhibits the catalysis and removes the catalyst from the cycle. The potential at which the electrocatalyzed reduction of CO_2 proceeds is determined by the potential at which the $[Ni^{I}L\text{-}CO_2H]^{2+}$ intermediate (see lower left hand side of Scheme 3) accepts electrons from the electrode. This potential is not affected by substitution on the cyclam ring, as shown by comparison of $[Ni(cyclam)]^{2+}$ and $[Ni(TMC)]^{2+}$ (TMC = tetra-*N*-methylcyclam) (**5**) as catalysts [93]. However, in

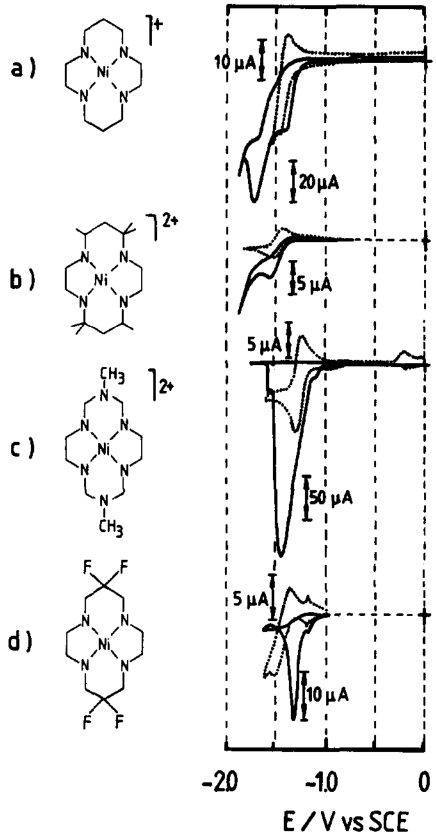
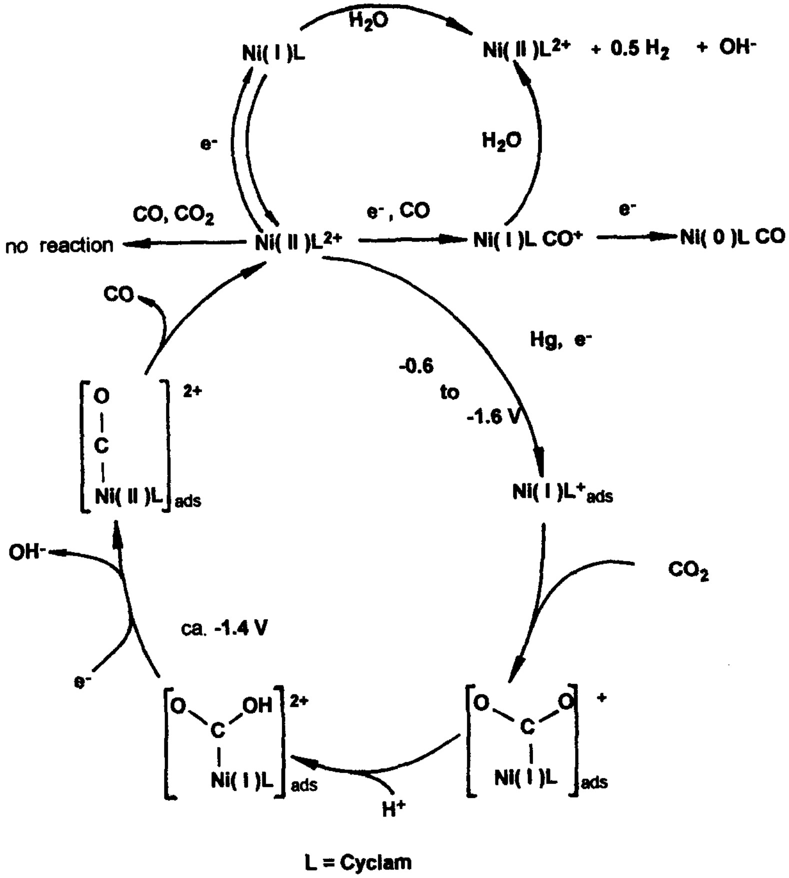


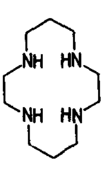
Fig. 1. Cyclic voltammograms of cyclotetradecane derivative complexes in N_2 (·····) and CO_2 (——): (a) glassy carbon electrode; 0.1 M $NaClO_4$ (pH 6.2), 0.1 V s^{-1}; (b) hanging mercury drop electrode; acetonitrile water, 0.1 M $NaClO_4$, 0.02 V s^{-1}; (c) hanging mercury drop electrode; acetonitrile water, 0.1 M $NaClO_4$, 0.1 V s^{-1}; (d) glassy carbon electrode; 0.5 M Na_2SO_4, 0.2 V s^{-1}.

some cases the catalytic activity of [NiL] (L = 5,7,7,12,14,14, hexamethyl-1,4,8,11-tetraaza-cyclotetradecane) (**6**) can be strongly decreased (Fig. 1(b)).

Rotating-copper-disk electrode techniques have been used to evaluate the efficiency of the nickel macrocyclic catalyst for the reduction of CO_2 to CO. Studies have been performed using Ni(diazacyclam)$^{2+}$ (diazacyclam = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclodecane) (**7**), a complex derived from cyclam, which appears to be more active than [Ni(cyclam)]$^{2+}$ under the same conditions Fig. 1(c) [15,96]. These results are consistent with a mechanism proposed by other authors [15,22,73]. Also, in an ab-initio MO–SDCI study of model complexes of the intermediates in the electrochemical reduction of CO_2 catalyzed by $NiCl_2$(cyclam) [97], calculations of several Ni^I- and Ni^{II}-CO_2 complexes indicate that CO_2 can coordinate to $Ni^IF(NH_3)_4$, yielding a stable Ni-CO_2 complex (**8**), but not to $[Ni^{II}F(NH_3)_4]^+$ $[Ni^{II}F(NH_3)_4]^+$



Scheme 3.



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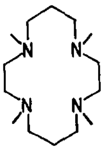

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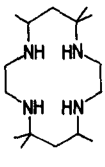

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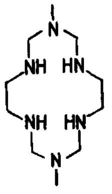

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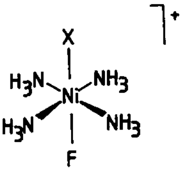
or $[Ni^I(NH_3)_5]^+$ [95]. The HOMO of $Ni^IF(NH_3)_4(n^1\text{-}CO_2)$ is largely the oxygen pπ orbital and lies at a higher energy than the HOMO (nonbonding π orbital) of the uncomplexed CO_2. In addition, the electron density increases around the oxygen atom upon CO_2 coordination. As a result, the coordinated CO_2 in $Ni^IF(NH_3)_4(n^1\text{-}CO_2)$ is activated with regard to electrophilic attack and is expected to undergo facile protonation. MO calculations also show that the second one-electron reduction can easily occur in the protonated species $[NiF(NH_3)_4(CO_2H)]^+$, yielding the triplet state $[NiF(NH_3)_4(CO_2H)]$, but cannot occur in the unprotonated species $NiF(NH_3)_4(CO_2)$ (**8**). The second reduction significantly weakens the C—OH bond, which suggests that OH^- easily dissociates from $[NiF(NH_3)_4(CO_2H)]$, yielding the triplet state of $[Ni^{II}F(NH_3)_4(CO)]^+$. The CO bond to Ni(II) is calculated to be weak, which suggests that CO easily dissociates from Ni(II). All these results support a reaction mechanism proposed previously [15] for the reduction of CO_2 electrocatalyzed by $NiCl_2$(cyclam).



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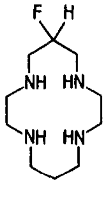
A series of new mono-, di- and tetrafluorinated cyclams (**9**, **10**, **11**) have recently been prepared. The electrocatalytic reduction of CO_2 showed that the efficiency of $(CO + H_2)$ product yields and the H_2/CO selectivity depend upon the number of fluorine atoms available. The tetrafluorinated complex shows more efficiency and selectivity at potentials lower than those measured for some nonfluorinated cyclam complexes [98]. Fig. 1(d) shows the results obtained for the 3,3,10,10-tetrafluorocyclam complex.



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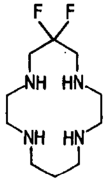

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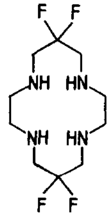

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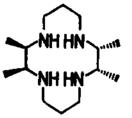
The CO yield decreases as the number of fluorine atoms increases [98]. However, at a potential of −1.10 V, $[Ni^{II}$(3,3,10,10-tetrafluoro-cyclam)]$(ClO_4)_2$ showed more efficient selective catalytic activity than the nonfluorinated [Ni(cyclam)]Cl_2 complex. The perchlorate complex may have a higher catalytic efficiency than the chloride complex at a higher potential (−1.3 V). Recent studies of the stereochemical effect of substituents on the electrocatalytic reduction of CO_2 have shown that the complexes RSSR-Ni(2,3,9,10-tetramethyl-cyclam$)^{2+}$ (**12**), RRSS-Ni(2,3,9,10-tetramethyl-cyclam$)^{2+}$ (**13**) and Ni(5,12-dimethyl-cyclam$)^{2+}$ (**14**) in aqueous KCl solution display increases in the catalytic current by a factor of 50–100, with the current densities of the RRSS-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ and Ni(5,12-dimethyl-cyclam)$^{2+}$ complexes being higher than that observed for Ni(cyclam)$^{2+}$ [99].



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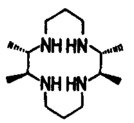

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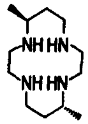

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Thus these complexes appear to be "better" catalysts than Ni(cyclam)$^{2+}$ in terms of their larger catalytic currents and more positive potentials. Hydrogen and formate production is less than 1.5% of the CO for each mole of complex. However, the geometric isomer RSSR-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ (**12**) shows a lower catalytic activity because the axial methyl group may sterically hinder CO_2 coordination.

Catalytic activity has not been observed in aprotic solvents because the mechanism (Scheme 3) requires a proton source. Experimental observations have been reported for Ni(cyclam)$^{2+}$ (**4**) in dimethylsulfoxide and for RSSR-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ (**12**), RRSS-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ (**13**) and Ni(5,12-dimethyl-cyclam)$^{2+}$ (**14**) in acetonitrile [100].

3.2.2. Porphyrin complexes

Metalloporphyrins are reported to be active catalysts in the electroreduction of CO_2 to CO in aqueous and nonaqueous media [101]. Cobalt(II)-tetraphenylporphyrin (Co^{II}tpp) (**15**), fixed on glassy carbon electrodes using 4-aminopyridine, is active toward the electroreduction of CO_2 to CO at potentials 100 mV more positive than water-soluble cobalt(II) porphyrins [102,103]. Fig. 2(a) shows cyclic voltammograms for the electrodes in a phosphate buffer solution at pH 6.86 saturated with N_2 or CO_2. No Co^{II}tpp/Co^{I}tpp redox peak was observed. A pronounced increase in the cathodic current was observed in CO_2-saturated solution at potentials 100 mV more positive than those obtained with water-soluble Co^{II}porphyrins. These results are consistent with the hypothesis that Co^{I}tpp, generated by the electrode reaction, catalyzes the reduction of CO_2. The electrolysis products were CO and H_2, and the overall turnover number (**15**) exceeded 10^5, in contrast with other systems in which the value is limited to 10^2 [22,103,104].

Water-soluble cobalt porphyrins have recently been used in some studies and exhibit some catalytic activity [105,106]. For example, when tetraphenyl-porphyrin (**15**) and octamethyl-phorpyrin complexes are used, CO is obtained catalytically, whereas palladium and silver porphyrins in dichloromethane produced oxalate. However, demetallation of the complexes rapidly deactivates the catalyst [105,106]. In these cases, the catalytic process was interpreted in terms of the anion radical species of the reduced state of the Pd(II) and Ag(II) porphyrins rather than the Pd(I) and Ag(I) states [107].

Tetraphenylporphyrin iron(III) chloride, with basket-handle of the picket-fence type with secondary amide groups in close vicinity to the porphyrin ring (**16**),

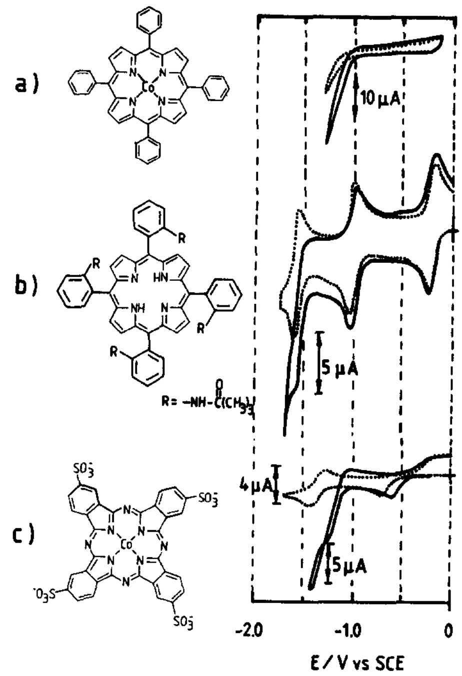
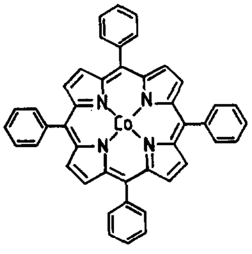


Fig. 2. Cyclic voltammograms of porphyrin and phthalocyanine derivative complexes in N_2 (·····) and CO_2 (——): (a) porphyrin fixed on a glassy carbon electrode; phosphate buffer (pH 6.86), 0.001 V s^{-1}; (b) glassy carbon electrode; 0.1 M dimethylformamide; $(C_2H_5)_4NClO_4$, 0.1 V s^{-1}; (c) hanging mercury drop electrode; 0.1 M $(C_2H_5)_4NClO_4$, 0.1 V s^{-1}.



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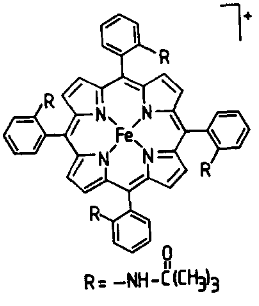

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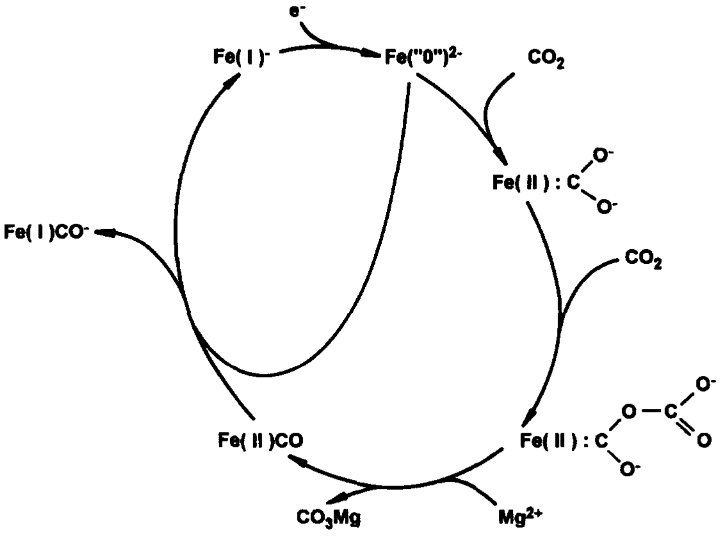
catalyze the electrochemical reduction of CO_2 to CO. Fig. 2(b) shows the cyclovoltammetric wave related to the formation of an Fe(0) species [107].

The porphyrin is rapidly consumed in these processes, and the catalysis stops after a small number of cycles. The degradation of the porphyrin appears to be the result of progressive saturation of the ring through carboxylation and/or hydrogenation. However, the addition of Mg^{2+} or other Lewis acids triggers a spectacular increase in the catalytic efficiency and the stability of the catalyst [107]. Also, lowering the temperature increases catalytic efficiency. Catalysis by the complex has been rationalized in terms of the introduction of one molecule of CO_2 into the coordination sphere of the iron atom. A carbene-type complex appears as a product when an electron pair is transferred from the iron porphyrin to the CO_2, as shown in Scheme 4. At low temperatures, the second step is the addition of another molecule of CO_2 in an acid–base type manner. The C—O bond of the first CO_2 molecule is then broken, forming the $Fe^{II}CO$ complex and a carbonate ion. In the same manner, Mg^{2+} ions can participate earlier in the breaking of the C—O bond. The stability of $Fe^{I}CO$ complex is temperature dependent, and its dissociation becomes more difficult as the temperature is decreased.



Scheme 4.

3.2.3. Phthalocyanine complexes

Several metallophthalocyanines have been reported to be active toward the electroreduction of CO_2 [108–111]. Modified electrodes have been employed for this purpose [68]. In one case, metallophthalocyanines deposited onto electrode surfaces have been used with aqueous solutions [15]. Polymeric complexes either immobilized on carbon electrodes [69–71] or incorporated in coated Nafion® membranes [13,72] have also been employed. The mechanism of catalysis for these systems has yet to be investigated (see below).

Cobalt phthalocyanine has been reported to be one of the most active phthalocyanines for CO_2 reduction [109,110,112,113], and the mechanism of the reduction in aqueous solution is believed to involve cobalt hydride intermediates [85]. Fig. 2(c) shows cyclic voltammograms for cobalt tetrasulfophthalocyanine in dimethylsulfoxide under N_2 and CO_2. The results were interpreted in terms of the formation of a CO_2 adduct with the reduced phthalocyanine complex [114].

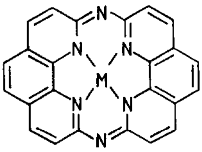
When cobalt and nickel phthalocyanines are used as electrocatalysts high yields of CO are obtained [108,110,111,115], although another study indicates that formic acid is the main reduction product [110]. When tin, lead and indium phthalocyanines are used, the main products are formic acid and H_2 [115], while for copper, gallium and titanium phthalocyanines the main products are CO and hydrogen but methane is also produced with a good yield (about 30%) [115]. Iron, zinc and palladium phthalocyanines also give CO as the leading reduction product, but in a lower yield compared with those obtained with cobalt and nickel phthalocyanines. Hydrogen is exclusively obtained with magnesium, vanadium, manganese and platinum derivatives and with the free base [107]. These distributions of products (and current efficiencies) depend strongly on the chemical properties of metal and ligand [115] and suggest that the mechanism of CO_2 reduction is different for each group. The mechanism for producing a particular product may be determined by the interaction between the phthalocyanine ring, the central metal and CO_2 or CO molecules.

Reaction mechanisms are highly speculative at this stage. A general mechanism is shown in Scheme 2. CO_2 is coordinated to the metal center, i.e. a nucleophile, by its electrophilic carbon. The isolation and characterization of CO_2 and CO adducts under different experimental conditions have recently been reported [16,43,44,114]. Semiempirical calculations have also contributed to the elucidation of the mechanism. For example, attempts have been made to correlate energy levels in metallophthalocyanines with their electrocatalytic activity [116]. Such catalytic activity in phthalocyanine and tetrasulfonated phthalocyanine complexes appears to be closely related to the possibility of coordinating extra-planar ligands. A factor controlling the binding of these ligands to the metal is the relative energy between the d orbitals of the metallophthalocyanine and the frontier orbital of the extra-planar ligand.

Ab-initio calculations of the coordination of CO_2 to several metals have recently been reported [117]. The relative stability of different modes of CO_2 coordination was calculated. One factor in the bonding between metal atoms and CO_2 is that the ground state has the maximum spin electron configuration. Other high-spin states, which only differ from the ground states by electron permutations within the non-bonding d subshell, must be very close to the ground state. The spin populations show a transfer of one metal valence electron to the CO_2 group, i.e. into a MO largely localized at the sp-hybridized atomic orbital of the carbon atom. Differences in the products of electrocatalysis (CO or CH_4 with some metallophthalocyanines and HCOOH with others) are rationalized on the basis of the electronic configuration of the metal atom. The reduction of CO_2 to CO is attributed to the strongly electron-donating HOMO of $[MPc]^{n-}$. This orbital, which derives from the electron-accepting LUMO of neutral MPc, spreads over the nitrogen atoms surrounding the metal atom M. the final step in the generation of CO takes place when it is rapidly separated from the metal M if this metal has a doubly occupied $2a_{1g}$ (dz^2) orbital. However, if the CO molecule is bound to the metallic atom by σ-bonding, the reduction may proceed up to the CH_4 product. Electron occupation of the LUMO by ionization does not take place in metals with outermost s or p electrons and extensive reduction to CO may not be possible. Electron transfer from MPc to CO_2 will end in CO_2^-, followed by separation of HCOOH instead of CO. In the "carbon dioxide complex" the anion CO_2^- is bent with an angle O—C—O equal to 134° and C is probably σ-bonded using the dz^2 or pz orbitals of M [118].

3.2.4. Biphenanthrolinic hexaazacyclophane complexes

Little is known about other systems containing extended π-electron orbitals and differing from the phthalocyanines and porphyrins. Since hexaazacyclophanes can be considered as relatives of the phthalocyanines and porphyrins, they may also be catalysts in numerous reactions. Preparative procedures for some of the azacyclophanes have been reported [119–124]. Recent studies of the chemical properties of azacyclophanes (**17**), which are hexaazacyclophane macrocyclic complexes derived from 1,10-phenanthroline, demonstrated that they are promising catalysts for CO_2 reduction.



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Large-yield preparations of this hexa-azamacrocyclic ligand, which is a diaza-bridging biphenanthrolinic macrocyclic ligand, and its Cu(II), Ni(II) and Co(II) complexes, have been reported [125]. Electrochemistry in a CO_2 atmosphere in dimethylformamide [126] demonstrates a high electrocatalytic activity for the reduction of CO_2 (Fig. 3(a)). The waves for CO_2 reduction mediated by these complexes, observed at about −0.80 V vs. SCE occur at the most positive potentials recorded for these electrocatalytic processes [127]. Reduction of CO_2 occurs close to the region involving the metal reduction process. Fig. 3(b) shows that the current intensity remains constant during prolonged electrolysis of the Ni derivative in CO_2 at the catalytic peak potential; however, in N_2 the same complex shows normal coulometric behavior involving one electron. The reduction products have been analysed by examination of the current ratios and comparison with other systems, but the results are not yet well understood [126]. Pulse radiolysis studies [126,128] suggest that CO_2 adducts could be formed during the reduction process observed in the Cu(II) complex. Semi-empirical self-consistent field and CI calculations of the INDO type have recently been applied to the analysis of the electronic transitions of **17** [127,129]. The results obtained confirm the activity of the structures toward electrochemical reduction processes involving the metal center.

4. Macrocyclic ligands related to macromolecular functions

Advances in the design of structures which show combinations of simple complexes and complicated free ligands (or complexes) have appeared in the literature in recent

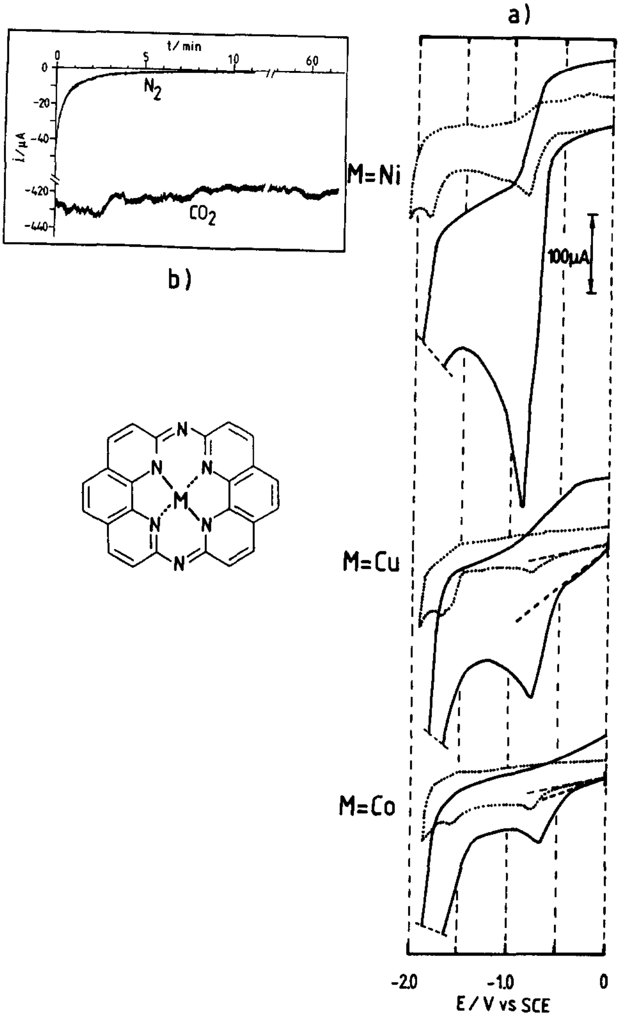
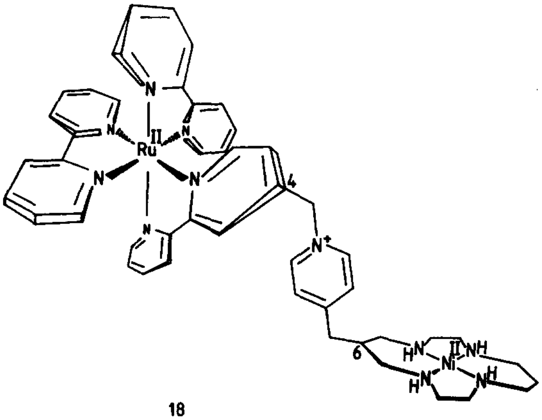


Fig. 3. Electrochemistry of complexes of hexaazacyclophane (17): (a) cyclic voltammograms at 0.2 V s^{-1} in N_2 (·····) and CO_2 (——); (b) intensity–time curves for the electrolysis of dilute solutions of 17 (M = Ni) at the first cathodic peak potential in (a).

years [127,130–134]. These assemblies, in which several subunits are linked together through noncovalent interactions, have been defined as supramolecular systems. The behavior observed for these superstructures can be described in terms of basic concepts of supramolecular chemistry [134], i.e. they act in molecular recognition, have supramolecular reactivity and transport, and show self-organizing tendencies with a positive cooperative display [135]. In this sense, coordinatively linked multicenter systems can be classified as supramolecular coordination compounds.

During the last 100 years coordination chemists have produced hundreds of metalcentered systems, many with redox activity, whose electrode potential can be conveniently modulated by synthetic modification of the coordination framework. More sophisticated systems, which are able to exchange a specified number of electrons, according to a predetermined sequence, at desired potential values, can now be prepared according to the principles of supramolecular chemistry. Moreover, the use of metal centers as structural elements allows the topology of the multi-electron redox systems to be controlled quite easily so that the redox sites can be placed in chosen positions at predetermined distances [136].

A new bifunctional super molecule (**18**) has recently been synthesized and its redox and CO_2 catalytic properties have been investigated [137]. Although this process induced reductive photocleavage of the supermolecule, catalytic studies show that twice the amount of CO is produced compared with the multimolecular system composed of $Ru(bpy)_3^{2+}$, pyridinium salt and Ni^{II}-cyclam.



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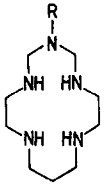

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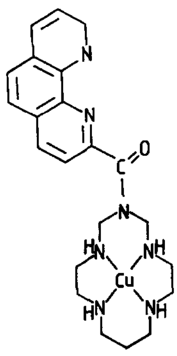
Functionalized azacyclam complexes of Ni(II) (**19**), where R is $-COCH_3$, $-COC_6H_5$ etc., have been prepared [138]. These Ni(II) azacyclam complexes catalyze the electroreduction of CO_2 with an efficiency equivalent to that of $[Ni^{II}(cyclam)]^{2+}$ (**15**), indicating that replacement of a $-CH_2$ group in the ligand backbone by an amide residue does not seriously alter the cyclam-like donor set (as far as the interaction with CO_2 is concerned) and does not disturb the catalytic process. Such a high efficiency is related to the structural features of the cyclam and azacyclam framework, i.e. a 14-membered cycle forming a 5, 6, 5, 6 sequence of chelate rings. Even small deviations from such a geometrical arrangement cause the electrocatalytic effect to be drastically reduced or completely lost. The electron-withdrawing effect of amido groups reduces the potential of the Ni^{II}/Ni^{I} couple; CO_2 is reduced to CO at a distinctly less negative potential than that observed when $Ni^{II}(cyclam)^{2+}$ is used as an electrocatalyst. Systems favoring the formation of the Ni(I) oxidation state are expected to behave as efficient electrocatalysts for CO_2 reduction. In this connection, Ni(II) complexes of some fluorinated cyclams, with Ni^{II}/Ni^{I} potentials less negative than that for $Ni^{II}(cyclam)^{2+}$, work well as catalysts for CO_2 reduction [139].

The effect of attaching a metal center to a phenanthroline backbone, as shown in **20**, has also been investigated. These compounds, where metal complexes function as ligands, can be defined as supercomplexes and belong to the domain of supramolecular coordination chemistry [140]. Analogously, a pyridine subunit has been attached to a metallocyclam fragment.



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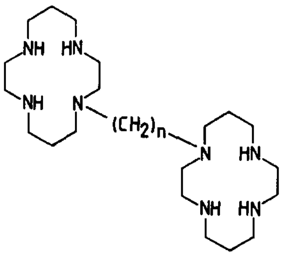

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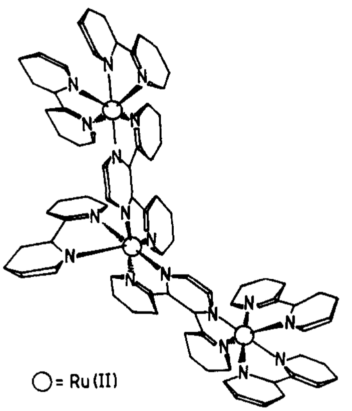
Covalent linking of two cyclam subunits (**21**) has produced a new class of binucleating ligands (biscyclams) which behave as ditopic receptors for transition metal ions, hosting two equivalent redox-active metal ions for example [136].

Although the scope of this review is restricted to macrocyclic structures, some complementary aspects of superstructures which are potentially useful in the electrochemical or photochemical activation of CO_2 should be mentioned. Thus the assembly of molecular components which possess specific properties is currently attracting much attention as a strategy for obtaining advanced materials. Components with suitable redox potentials and/or excited state levels are fundamental building blocks for the design of photochemical molecular devices capable of performing important functions such as information storage, solar energy conversion and multi-electron catalysis. M(II) complexes of polypyridine-type ligands can be used as building blocks to synthesize redox-active and luminescent supramolecular (polynuclear) metal complexes where electron and/or energy-transfer processes can be induced by light [141]. Compounds **22** and **23** show some examples of supercomplexes of this type [132,142,143].



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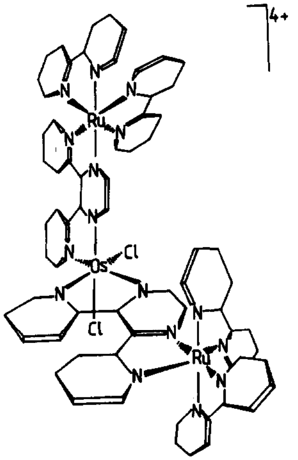
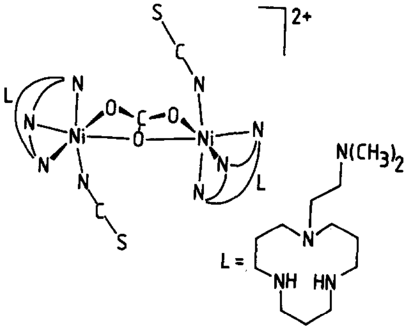


23

The electrochemistry of complex **23** is unique among polymetallic systems as a result of the central L_2OsCl_2 core. Unlike mono- and bimetallic Os and Ru complexes prepared previously, the metal-based Os^{III}/Os^{II} oxidation in these complexes varies as a function of the bridging ligand employed. The bridging ligands are only reduced by one electron prior to reduction of the bipyridyl ligands owing to the influence of the electron-rich L_2OsCl_2 center. The terminal ruthenium centers of **23** oxidize at different potentials, indicative of long-range communication through the L—Os—L framework. The utilization of synthetic variations and the stability of several oxidation states in these complexes has made it possible to clarify electrochemical data for these supramolecular complexes [144].

Some superstructures are able to sequester CO_2 [145]. Complex **24** has the structure of an antiferromagnetically coupled μ-carbonato-bridged bis-nickel(II) complex which contains the pendant-arm macrocycle 1-(3-dimethylaminopropyl)-1,5,9-triaza-cyclododecane*N*$_3$. This system sequesters CO_2 from air after the addition of thiocyanate ion [145].



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5. Mechanistic aspects of CO_2 photoreduction

Macrocyclic complexes have been used as catalysts for the photochemical reduction of CO_2. This photoinduced process is generally initiated by the oxidative quenching of an excited state S* by a catalyst C

$$S + h\nu \rightarrow S^* \xrightarrow{+C} S^+ + C^- \tag{4}$$

or by the reaction of a photoreduced species with the catalyst. The photoreduced species may be an electron relay R

$$S + h\nu \rightarrow S^* \xrightarrow{+R} S^+ + R^{\cdot -} \tag{5}$$

$$R^{\cdot -} + C \rightarrow R + C^- \tag{6}$$

or the same photosensitizer

$$S + h\nu \rightarrow S^* \xrightarrow{+R} S^- + R^{\cdot +} \tag{7}$$

$$S^- + C \rightarrow S + C^- \tag{8}$$

The quantum yield of CO_2 reduction is very low ($\phi \leqslant 10^{-3}$) in most of the currently investigated examples, or the photochemical reaction has been driven by UV light.

Ascorbate has been used as a reductive quencher of the metal-to-ligand charge transfer (MLCT) excited state in $Ru(bipy)_3^{2+}$. Complexes of Ni(II) with [12]ane-1,4,7,10-N_4 and cyclam were photoreduced by $Ru(bipy)_3^+$ in aqueous solutions (pH 5) and 0.1 M ascorbate [146]. Both nickel compounds reduce CO_2 with the same quantum yield ($\phi \approx 6 \times 10^{-4}$). Products of the process photocatalyzed $Ni([12]ane\text{-}1,4,7,10\text{-}N_4)^{2+}$ are formate ($\phi \approx 1.9 \times 10^{-4}$) and CO ($\phi \approx 4.5 \times 10^{-4}$). In contrast, only CO was detected when $Ni(cyclam)^{2+}$ was the catalyst. The yield of H_2 (a product of the irradiation of $Ru(bipy)_3^{2+}$ in ascorbate solutions) is negligible in solutions containing these macrocyclic complexes. Nickel hydride species, generated after the reduction of Ni(II) to Ni(I), have been proposed to be intermediates which react with CO_2 [147]. In this mechanism, CO and formate result from the insertion of CO_2 into the Ni—H bond. A pulse radiolysis study has shown that Ni^IL complexes, structurally related to $Ni(cyclam)^+$, undergo transformations which could be interpreted in terms of a proton transfer to Ni(I) [148]:

$$Ni^IL + HX \underset{+X^-}{\overset{-X^-}{\rightleftarrows}} [LNi^I\text{–}H^+] \rightleftarrows [LNi^{II}\text{–}H] \rightleftarrows [LNi^{III}\text{–}H^-] \tag{9}$$

$H^{\cdot}$ atoms generated by pulse radiolysis react with these Ni^{II} complexes to give Ni^I products instead of the Ni^{III}–H hydride, i.e. the final product in Eq. (9):

$$Ni^{II}L + H^{\cdot} \rightarrow Ni^IL + H^+ \tag{10}$$

Ni(II) macrocyclic complexes with a NH_2-pendant donor group [144], or covalently attached to $Ru(phen)_3^{2+}$ and $Ru(bipy)_3^{2+}$ [149], could improve the yield of CO_2 photoreduction relative to the yield of H_2 photogeneration. Attachment of the Ru(II) sensitizer to the Ni(II) complexes $[Ru(1,10\text{-phen})_2(5'\text{-}(N\text{-methylen-}Ni^{II}(cyclam)\text{-}1,10\text{-phen})]^{4+}$ and $[Ru(2,2'\text{-bipy})_2(6\text{-}(N\text{-methylen-}Ni^{II}(cyclam)\text{-}2,2'\text{-bipy})]^{4+}$ does not produce a substantial increase in the overall quantum yield. Catalysis of the CO_2 photoreduction with the 1,10-phen derivative gives a higher yield of CO than that with $Ru(2,2'\text{-bipy})_3^{2+}$. In addition, the 1,10-phen complex undergoes a larger number of turnovers than the 2,2′-bipy complex. The lifetime of the $[Ru(2,2'\text{-bipy})_2(6\text{-}N\text{-methylen-}Ni^{II}(cyclam)\text{-}2,2'\text{-bipy})]^{4+}$ is very short compared with that of $Ru(bipy)_3^{2+}$. The relative decrease in the lifetime has been associated with energy transfer from the MLCT state of Ru(II) to the Ni(II) macrocycle [5,150]. An increased rate of conversion of the MLCT to an upwardly placed ligand field state has also been considered to be responsible for the short lifetime of the charge transfer state [6]. Stabilization of the ligand field state and/or a decrease of the reorganization energy in the excited state conversion has been associated with enlarged Ru—N bonds. Such a nuclear distortion and the resultant decline in ligand field strength have been related to steric hindrance in the binuclear complex.

The slugishness of electron transfer reactions of nickel macrocycles may hamper their catalytic activity [18]. Self-exchange electron transfer rate constants of Ni(II)/Ni(I) macrocycles in aqueous solutions range from 10^4 to 10^8 M^{-1} s^{-1} [88]. Since the value of the rate constant increases with the number of imino groups coordinated to the nickel atom, the exchange $Ni(cyclam)^{2+/+}$ is affected by the largest nuclear reorganization. In this regard, structural factors of the macrocycle that can be used to accelerate the rate of electron transfer must be weighed against possible restrictions dictated by the mechanism of catalyzed CO_2 reduction described above.

Although metal–ligand distances undergo a large change when the oxidation state changes from Ni(II) to Ni(I), they are not significantly changed by the reduction of Co(II) to Co(I) [7]. The corresponding reorganization energies make the electron transfer reactions of the cobalt macrocycles faster than those of similar nickel complexes [7]. The mechanism of the CO_2 photoreduction catalyzed by cobalt macrocyclic complexes has been investigated in a number of studies. A series of 14-membered cobalt and nickel macrocycles were investigated using *p*-terphenyl (TP) [7]. The radical anion of *p*-terphenyl ($TP^{\cdot -}$) reduces CO_2 to formate ($\phi \approx 0.072$ at 313 nm) in triethylamine (TEA) + dimethylformamide. Since the anion radical also undergoes Birch reduction, the photocatalyst is limited to four turnovers. The presence of $CoII(cyclam)^{2+}$ in the reaction mixture prevents degradation of *p*-terphenyl and increases the overall quantum yield for CO_2 photoreduction, i.e. $\phi \approx 0.25$ at 313 nm for combined CO and HCO_2^-. The mechanism proposed for the catalyzed photoreduction of CO_2 is shown below, where $[14]aneN_4$ represents a generic derivative of cyclam [7].

$$TP^{\cdot -} + Co^{III}([14]aneN_4)(TEA)_2^{3+} \rightarrow TP + [Co^{II}([14]aneN_4)(TEA)]^{2+} + TEA \tag{7}$$

$$TP^{\cdot -} + [Co^{II}([14]aneN_4)(TEA)]^{2+} \rightarrow TP + Co^{I}([14]aneN_4)^{+} + TEA \tag{8}$$

$$CO_2 + Co^I([14]aneN_4)^+ \rightarrow [Co^I([14]aneN_4)CO_2]^+ \qquad (9)$$

$$TEA + [Co^I([14]aneN_4)CO_2]^+ \rightleftarrows [Co^{III}([14]aneN_4)(CO_2^{2-})(TEA)]^+ \qquad (10)$$

$$[Co^{III}([14]aneN_4)(CO_2^{2-})(TEA)]^+ + H^+ \rightleftarrows [Co([14]aneN_4)(CO_2H)(TEA)]^{2+} \qquad (11)$$

$$[Co([14]aneN_4)(CO_2H)(TEA)]^{2+} + TP^{\cdot -} \rightarrow [Co^{II}([14]aneN_4)(TEA)]^{2+} + CO + OH^- + TP \qquad (12)$$

Steric hindrance by groups attached to the macrocycle reduces the accessibility of CO_2 and other molecules to the cobalt or nickel center. In the mechanism given above (Eqs. (9)–(12)) steric hindrance will directly affect the rates of Eqs. (9) and (10). Indeed, the cobalt complex of 1,4,8,11-Me_4-cyclam failed as a catalyst because steric hindrance prevented the formation of hexacoordinated species. Another factor is that methylation of all the amino groups in the macrocycle elevates the potential of the Co(III)/Co(II) couple above 1.2 V, which makes an unfavorable contribution to the rates of Eqs. (7) and (8). TP/M(cyclam)$^{2+}$ (M = Ni, Zn, Fe, Cu) also failed to photocatalyze CO_2 reduction. In the Ni(II)-based system, the Ni(III)/Ni(II) potential may be too high. Since Ni(cyclam)$^{2+/+}$ exchange takes place with a rate constant of only $10^4\ M^{-1}\ s^{-1}$ [8], reorganization in the Ni(II)/Ni(I) pair may prevent sufficiently fast electron transfers.

Specific reactions in the mechanism (Eqs. (7)–(12)) were investigated by pulse radiolysis of Co(Me_6[14]4,11-dieneN_4)$^{2+}$ solutions [151]. This allowed the kinetics and thermodynamics of CO_2, CO and H^+ coordination to Co(I) and the formation of hydride complexes to be established. Hydride formation by protonation of Co(I) complexes or by reactions of Co(II) with hydrogen atoms is favored below pH 7:

$$\begin{array}{l} Co(N\text{-}meso\text{-}[14]4,11\text{-}dieneN_4)^+ + H^+ \\ \qquad\qquad \searrow \\ \qquad\qquad\qquad Co(N\text{-}meso\text{-}[14]4,11\text{-}dieneN_4)(H)^{2+} \\ \qquad\qquad \nearrow \\ Co(N\text{-}meso\text{-}[14]4,11\text{-}dieneN_4)^{2+} + H^{\cdot} \end{array} \qquad (13)$$

$$Co(N\text{-}rac\text{-}[14]4,11\text{-}dieneN_4)^+ + H^+ \rightarrow prim\text{-}Co(N\text{-}meso\text{-}[14]4,11\text{-}dieneN_4)(H)^{2+} \qquad (14)$$

$$Co(N\text{-}rac\text{-}[14]4,11\text{-}dieneN_4)^{2+} + H^+ \rightarrow sec\text{-}Co(N\text{-}meso\text{-}[14]4,11\text{-}dieneN_4)(H)^{2+} \qquad (15)$$

The addition of CO_2 to Co(I) and the reaction of Co(II) with $CO_2^{\cdot -}$ are rapid and resemble the reactions leading to the formation of hydride complexes (Eqs. (13)–(15)):

$$\begin{tikzcd} \mathrm{Co}(N\text{-}meso\text{-}[14]4{,}11\text{-dieneN}_4)^+ + \mathrm{H}^+ \arrow[dr] & \\ & \mathrm{Co}(N\text{-}meso\text{-}[14]4{,}11\text{-dieneN}_4) + \mathrm{CO}_2 \\ \mathrm{Co}(N\text{-}meso\text{-}[14]4{,}11\text{-dieneN}_4)^{2+} + \mathrm{CO}_2^{\cdot -} \arrow[ur] & \end{tikzcd} \tag{16}$$

$$\mathrm{Co}(N\text{-}rac\text{-}[14]4{,}11\text{-dieneN}_4)^{2+} + \mathrm{CO}_2 \rightarrow prim\text{-}\mathrm{Co}(N\text{-}meso\text{-}[14]4{,}11\text{-dieneN}_4)(\mathrm{CO}_2)^+ \tag{17}$$

$$\mathrm{Co}(N\text{-}rac\text{-}[14]4{,}11\text{-dieneN}_4)^{2+} + \mathrm{CO}_2^{\cdot -} \rightarrow sec\text{-}\mathrm{Co}(N\text{-}meso\text{-}[14]4{,}11\text{-dieneN}_4)(\mathrm{CO}_2)^+ \tag{18}$$

Addition of CO to the $\mathrm{Co(Me_6[14]4,11\text{-}dieneN_4)^+}$ is also rapid and gives pentacoordinated species independent of isomer and solvent. Equilibration between these CO_2, CO and H^- complexes appears to proceed exclusively through the formation of Co(I) macrocycles. The addition of CO_2 to $\mathrm{Co}(N\text{-}rac\text{-}\mathrm{Me_6[14]4,11\text{-}dieneN_4})^+$ gives penta- and hexacoordinated complexes, with the latter form being dominant at low temperatures. In contrast, the hydride and the other two CO_2 isomers are hexacoordinated at all temperatures. Four different isomers of $\mathrm{Co(Me_6[14]4,11\text{-}dieneN_4)(CO_2)^+}$ and $\mathrm{Co(Me_6[14]4,11\text{-}dieneN_4)(CO_2)(CD3CN)^+}$ have been characterized in the temperature range from 25 to −75°C [152]. In the low-temperature regime, two isomers, one pentacoordinated and one hexacoordinated, show intramolecular hydrogen bonding between CO_2 and the hydrogen atoms in amino groups of the ligand. The overall stability of these isomers results from combined binding of CO_2 to the metal center through the electrophilic carbon and hydrogen bonding to the amino groups through the nucleophilic oxygen. The other two isomers are non-hydrogen-bonded forms.

Macrocyclic complexes have not been used to their full potential for the heterogeneous (pseudo-homogeneous) catalysis of CO_2 photoreduction. In the conventional technique, bipyridinium derivative is used as an electron relay after being reduced by an excited state. The reduced relay is used to charge a catalyst of colloidal Ru($[\mathrm{Ru}]_n$) or palladium deposited on TiO_2 [153,154]. Bicarbonate is reduced to formate by palladium hydride on the surface of the palladium activated catalyst [1]. Metal-to-ligand charge transfer states of the Ru(II) complexes $\mathrm{Ru(bipy)_3^{2+}}$, $\mathrm{Ru(phen)_3^{2+}}$ and $\mathrm{Ru(bipy)_2(pyMpym)^{2+}}$ have been used in the photoreduction of the charge relay [2]. A typical mechanism is shown below, where $\mathrm{RuL_3^{2+}}$ represents one of the Ru(II) complexes mentioned above and MPVS is N,N′-3-propylsulfonato-(3,3′-dimethyl)-4,4′-bipyridinium:

$$\mathrm{RuL_3^{2+}} + h\nu \xrightarrow{\phi} \mathrm{MLCT} \tag{23}$$

$$\mathrm{MLCT} + \mathrm{MPVS} \rightarrow [\mathrm{RuL_3^{3+}}, \mathrm{MPVS}^{\cdot -}] \tag{24}$$

$$[\mathrm{RuL}_3^{3+}, \mathrm{MPVS}^{\cdot -}] \rightarrow \mathrm{MPVS}^{\cdot -} + \mathrm{RuL}_3^{3+} \tag{25}$$

$$\mathrm{MPVS}^{\cdot -} + \mathrm{CO}_2 \text{ (and } \mathrm{H}^+) \xrightarrow{[\mathrm{Ru}]_n} \mathrm{MPVS} + \mathrm{CH}_4 \text{ (and } \mathrm{H}_2) \tag{26}$$

$$\mathrm{RuL}^{3+} + \mathrm{TEOA} \rightarrow \mathrm{RuL}^{2+} + \mathrm{TEOA}^{\cdot -} \tag{26}$$

Generation of the intermediate surface species $[\mathrm{Ru}]_n{=}\mathrm{CH}_2$ and $[\mathrm{Ru}]_n{-}\mathrm{CH}_3$ has been proposed in order to explain the formation of CH_4 from the reduction of CO_2. Charge separation yields from cage encounter complexes $[\mathrm{RuL}_3^{3+}, \mathrm{MVPS}^{\cdot -}]$ determine the overall efficiency of CO_2 reduction. Although the cage escape yield ($\phi \approx 1.4 \times 10^{-2}$) for $\mathrm{Ru(phen)}_3^{2+}$ is 1.5 times larger than that for $\mathrm{Ru(bipy)}_3^{2+}$, no charge separation is observed from pairs of the pyMpym complex. This makes $\mathrm{Ru(phen)}_3^{2+}$ the best of the three photosensitizers for CO_2 reduction.

Macrocyclic complexes of transition metal ions can be expected to satisfy the requirements for a useful charge-relay. In terms of preventing low efficiencies for CO_2 reduction because of a small cage separation yield, the prospect of combining the functions of photosensitizer and charge relay in a single macrocycle is appealing. In this regard, the phthalocyanines are known to undergo multiple electron reductions which change the oxidation states of the metal ion and the ligand [155]. Hydrogenation of the ligand in Mo(V) tetrasulfophthalocyanine can be driven by photochemical and electrochemical means. Since the reduction of the macrocycle can be reversed in the presence of colloidal Pt with liberation of H_2, the Mo(V) complex displays some of the properties expected for a charge relay [156]. The M(hexaazacycloplanes) (M = Cu(II), Ni(II), Co(II)) undergo one-electron reductions to species which can be regarded as complexes of the divalent metals with a coordinated radical [157]. In view of their electrochemical properties (summarized above) and interactions with CO_2, it is very possible that they will be able to perform the dual role of catalysts and relays.

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