Cobalt and Nickel Complexes of 2,2′:6′,2″:6″,2‴-Quaterpyridine as Catalysts for Electrochemical Reduction of Carbon Dioxide†

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The complexes $[Co(qtpy)(OH_2)_2][ClO_4]_2$ and $[Ni(qtpy)(MeCN)_2][ClO_4]_2$ (qtpy = 2,2′:6′,2″:6″,2‴-quaterpyridine) were prepared by treating qtpy with $Co(ClO_4)_2{\cdot}6H_2O$ and $Ni(ClO_4){\cdot}6H_2O$ respectively in acetonitrile. In acetonitrile both complexes show one reversible couple assignable as the $[M(qtpy)L_2]^{2+/+}$ couple {$E_{\frac{1}{2}}$ for $[Co(qtpy)(OH_2)_2]^{2+/+} = -0.67$ V; $[Ni(qtpy)(MeCN)_2]^{2+/+} = -0.79$ V *vs.* saturated calomel electrode, SCE}, one quasi-reversible couple assignable as $[M(qtpy)]^{+/0}$ ($E_{\frac{1}{2}} = -0.96$ for Co, −1.15 V for Ni) and one reduction wave at about −1.98 V *vs.* SCE assignable as reduction of [M(qtpy)] to $[M(qtpy)]^-$. Constant-potential electrolysis of a 0.2–0.4 mmol dm^{-3} solution of $[Co(qtpy)(OH_2)_2]^{2+}$ in the presence of CO_2 at −1.7 V resulted in the production of CO with a current efficiency of about 80%. At bulk concentration of $[Co(qtpy)(OH_2)_2]^{2+} \geqslant 0.2$ mmol dm^{-3}, electrodeposition of the cobalt complex occurs at −1.65 V *vs.* SCE to give a dark brown electroactive film on the electrode surface. The cobalt-modified electrode is catalytically active towards the electrochemical reduction of carbon dioxide both in acetonitrile and in water. Constant-potential electrolysis with the cobalt-modified electrode at −1.7 V in acetonitrile and at −1.3 V in water resulted in the production of CO with current efficiencies of about 35%. No film formation on the electrode was observed for $[Ni(qtpy)(MeCN)_2]^{2+}$ and its catalytic activity towards reduction of CO_2 is much less than that of the cobalt complex.

Many transition-metal complexes of 2,2′-bipyridine (bipy) and 2,2′:6′,2″-terpyridine are active photocatalysts and/or electrocatalysts for activation of small molecules such as carbon dioxide.[1–4] Relatively few studies[5] have been conducted on the catalytic behaviour of metal complexes of higher oligopyridines such as 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy). The difference in co-ordination behaviour of quaterpyridine from those of the lower oligopyridines might affect the binding of the central metal ion to substrates as well as the stability of the metal complex. Previous studies[6–8] on $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) revealed that adsorbed nickel(I) complex on the electrode surface plays an important role in the electrochemical reduction of CO_2. A recent study[9] on $[Ru(bipy)(CO)_2Cl_2]$ indicated that polymeric $[\{Ru(bipy)(CO)_2\}_n]$ film can be electrodeposited on an electrode surface and the resulting chemically modified electrode is active towards reduction of CO_2. Quaterpyridine, by virtue of its planar structure and hydrophobic character, might facilitate the adsorption and electrodeposition of complexes onto electrode surfaces. As cobalt and nickel complexes of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine are known to be active catalysts for the electrochemical reduction of carbon dioxide,[10–13] it might be interesting to study their quaterpyridine analogues. We therefore conducted an investigation on the electrocatalytic properties of the cobalt and nickel complexes of 2,2′:6′,2″:6″,2‴-quaterpyridine for reduction of CO_2.

Experimental

Materials.—The salt $Co(ClO_4)_2{\cdot}6H_2O$ was obtained from Strem Chemical Co. 2,2′:6′,2″:6″,2‴-Quaterpyridine and $[Ni(qtpy)(MeCN)_2][ClO_4]_2$ were synthesized by the literature methods.[14] Acetonitrile (Ajax) was distilled over CaH_2 before use. Tetra-*n*-butylammonium hexafluorophosphate (Electrometric grade, Southwestern Analytical Chemicals) was dried *in vacuo* at 80 °C for 24 h before used. High-purity CO_2 (⩾99.9%) was obtained from Hong Kong Oxygen Co. Other chemicals were of reagent grade obtained from Aldrich Chemical Co. and were used as received.

Synthesis of $[Co(qtpy)(OH_2)_2][ClO_4]_2$.—To a solution of $Co(ClO_4)_2{\cdot}6H_2O$ (0.25 g, 0.68 mmol) in acetonitrile (10 cm^3) was added 2,2′:6′,2″:6″,2‴-quaterpyridine (0.25 g, 0.80 mmol). The resulting mixture was warmed to 60 °C on a water-bath for 30 min. The solution changed from pink to orange-brown. Addition of diethyl ether resulted in the precipitation of $[Co(qtpy)(OH_2)_2][ClO_4]_2$ as a light brown powder (yield 70%). The structure of $[Co(qtpy)(OH_2)_2][ClO_4]_2$ was confirmed by X-ray crystallography in our laboratory to be identical to that of $[Co(qtpy)(OH_2)_2][NO_3]_2$ previously reported.[15] UV/VIS in MeCN [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 500 (50), 337 (12 800), 325(sh) (11 100), 298 (23 000) and 288(sh) (17 200). μ_{eff}(solid) = 3.79 μ_B at room temperature.

Physical Measurements.—The UV/VIS spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer, infrared spectra on a Nicolet Magna-IR 750 FTIR spectrometer. Magnetic susceptibility was measured by the Guoy method with mercury tetrathiocyanatocobaltate(II) as calibrant. Cyclic voltammetry was performed by a Princeton Applied Research model 273A potentiostat and a Kipp & Zonen XY recorder. A conventional two-compartment electrochemical cell was used. The glassy carbon electrode was treated by polishing with 0.3 μm alumina on a microcloth, sonicated for 5 min in deionized water and then rinsed with

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

acetonitrile. An Ag–AgNO$_3$ (0.1 mol dm^{-3} in MeCN) electrode was used as reference electrode; $E_{\frac{1}{2}}$ values are the average of the cathodic and anodic peak potentials for the oxidative and reductive waves. The $E_{\frac{1}{2}}$ of the ferrocenium–ferrocene couple measured in the same solution was used as internal reference, but all potentials in this report are quoted with respect to the saturated calomel electrode (the $E_{\frac{1}{2}}$ of ferrocenium–ferrocene was taken as 0.307 V *vs.* SCE[16]).

Constant-potential electrolysis was performed in a three-compartment cell. The working electrode was a graphite cloth obtained from Sigri Co. (Meitingen, Germany). A control experiment was always performed by electrolysing a blank solution saturated with CO$_2$ to compare with the experimental results. After completion of an electrolysis, gas samples was taken through a septum from the head-space above the solution in the working-electrode compartment and analysed by a Hewlett–Packard model 5890 series II gas chromatograph equipped with a thermal conductivity detector. A 6 ft × $\frac{1}{8}$ in stainless-steel column packed with 5 Å molecular sieves was employed in the analysis with helium as the carrier gas. Formate ions in the solution were analysed by the chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid) spot test[17] or by ion chromatography with Wescan ion chromatograph equipped with a Supelcogel C-610H column.

Results and Discussion

Synthesis and Spectroscopic Properties of the Complexes.—The synthesis, spectroscopic properties and crystal structure of $[Ni(qtpy)(MeCN)_2][PF_6]_2 \cdot MeCN$ have previously been reported by Constable *et al.*[14] It is a high-spin complex with a μ_{eff} of 2.9 μ_B at room temperature. Reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with qtpy in acetonitrile gave $[Co(qtpy)(OH_2)_2][ClO_4]_2$. Although the crystal structure of $[Co(qtpy)(OH_2)_2][NO_3]_2$ has been reported previously,[15] X-ray diffraction analysis was performed on $[Co(qtpy)(OH_2)_2][ClO_4]_2$ to confirm the structure of the cobalt complex prepared in acetonitrile. The structure of $[Co(qtpy)(OH_2)_2][ClO_4]_2$* was found to be identical to that of $[Co(qtpy)(OH_2)_2][NO_3]_2$. Magnetic susceptibility measurement showed that the Co^{II} is in a high-spin state. The measured μ_{eff} of 3.79 μ_B is close to the spin-only value of three unpaired electrons. The UV/VIS absorption spectra of both $[Co(qtpy)(OH_2)_2][ClO_4]_2$ and $[Ni(qtpy)(MeCN)_2][ClO_4]_2$ show intense absorption bands with λ_{max} at ≈336 and ≈295 nm assignable to the intraligand transitions of qtpy. For the cobalt(II) complex there is a weak and broad absorption with λ_{max} at 500 nm (Fig. 1). Presumably this is due to a d–d transition.

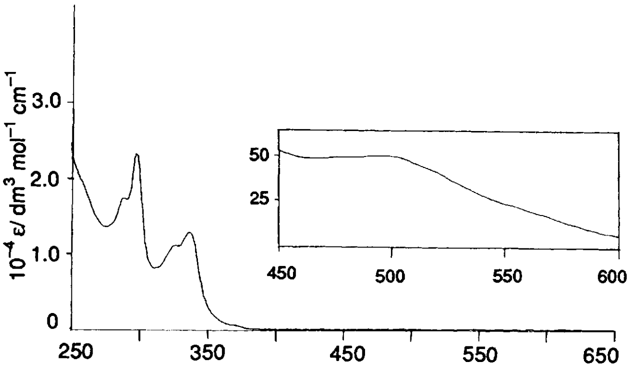

Fig. 1 The UV/VIS spectrum of $[Co(qtpy)(OH_2)_2]^{2+}$ in acetonitrile

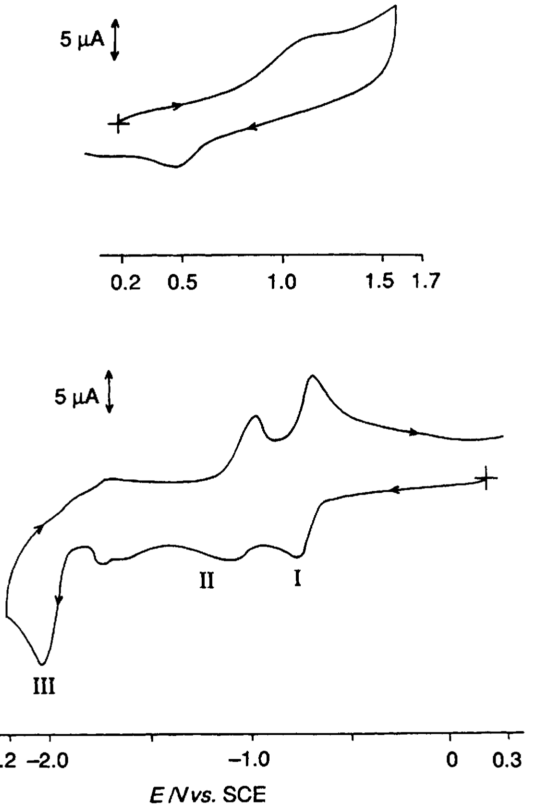

Fig. 2 Cyclic voltammogram of 0.15 mmol dm^{-3} $[Co(qtpy)(OH_2)_2]^{2+}$ in acetonitrile. Working electrode: glassy carbon (area 0.086 cm^2). Supporting electrolyte: 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate. Scan rate: 100 mV s^{-1}

Couple I: $[Co(qtpy)(OH_2)_2]^{2+} + e^- \rightleftharpoons [Co(qtpy)(OH_2)_2]^+$

$[Co(qtpy)(OH_2)_2]^+ \overset{\text{slow}}{\rightleftharpoons} [Co(qtpy)]^+ + 2H_2O$

Couple II: $[Co(qtpy)]^+ + e^- \rightleftharpoons [Co(qtpy)]$

Scheme 1

Voltammetry of the Metal Complexes in Acetonitrile.—The cyclic voltammogram of $[Co(qtpy)(OH_2)_2]^{2+}$ in acetonitrile is shown in Fig. 2. Oxidation of $[Co(qtpy)(OH_2)_2]^{2+}$ leads to a broad wave at 1.18 V *vs.* SCE. The corresponding reduction wave appears at 0.55 V. This quasi-reversible couple can be assigned as the Co^{III}–Co^{II} couple. Unlike $[Co(bipy)_3]^{2+}$,[18] the Co^{III}–Co^{II} couple of $[Co(qtpy)(OH_2)_2]^{2+}$ exhibits widely separated anodic and cathodic peaks. Upon reductive scan, a reversible couple (I) at −0.67 V *vs.* SCE assignable as the Co^{II}–Co^{I} couple is observed. Further reduction of $[Co(qtpy)(OH_2)_2]^+$ leads to a quasi-reversible couple (II) at −0.96 V assignable as the Co^{I}–Co^{0} couple. Constant-potential coulometry indicated that both couples I and II are one-electron reductions. Although they can be assigned as above, previous electrochemical studies[19] indicated that most redox processes of metal polypyridyl complexes have certain extents of ligand-centred character. The fact that the reductive wave of couple II is flattened and its cathodic peak current does not increase linearly with the square root of scan rate suggests this is not a purely diffusion-controlled process. Previous studies on the electrochemistry of $[Co(bipy)_3]^{2+}$ in acetonitrile[18] indicated that reduction of $[Co(bipy)_3]^+$ is accompanied by the loss of one bipyridine ligand. It is likely that reduction of $[Co(qtpy)(OH_2)_2]^+$ is also accompanied by a similar ligand dissociation reaction (Scheme 1). The above mechanism is supported by the observation that the ratio of the anodic peak current to the cathodic peak current (i_{pa}/i_{pc}) for couple I is much less than unity at slow scan rates (0.90, 0.85 and 0.82 at scan

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* The details of the crystal and molecular structure are available from C. M. Che upon request.

rate = 100, 20 and 10 mV s^{-1} respectively). Moreover, addition of a small amount of water to the solution would make couple I more reversible at slow scan rates while the size of couple II would become smaller and the shape more ill defined, which is consistent with the dissociation of a water ligand from the cobalt complex upon reduction of Co^{II} to Co^{I}. Further reduction of [Co(qtpy)] leads to an irreversible wave III at -1.98 V which can be assigned as the reduction of [Co(qtpy)] to [Co(qtpy)]$^-$. Wave III is probably a predominantly quaterpyridine-based reduction as the voltammetry of free quaterpyridine in acetonitrile also shows an irreversible reduction wave at -1.94 V *vs.* SCE.

The cyclic voltammogram of [Ni(qtpy)(MeCN)$_2$]$^{2+}$ (Fig. 3) shows one reversible couple at -0.79 V and one quasi-reversible couple at -1.15 V (labelled I′ and II′ respectively). Constant-potential coulometry indicated that both are one-electron couples. They can be assigned as Ni^{II}–Ni^{I} and Ni^{I}–Ni^{0} respectively. Similar to the cobalt complex, the cathodic peak current of couple II′ does not increase linearly with the square root of the scan rate and the electron transfer is likely to be accompanied by chemical reactions such as ligand dissociation. For the nickel(0) complex, an 18 e square planar structure is the most stable[20,21] and the most possible chemical reaction is the dissociation of the axial acetonitrile ligands (Scheme 2). Again this mechanism is supported by the ratio of anodic to cathodic peak currents (i_{pa}/i_{pc}) for couple I′ being less than unity at slow scan rate (0.95, 0.84 and 0.59 at v = 100, 20 and 5 mV s^{-1}). In addition, a small couple (labelled IV′) appears at -1.28 V near couple II′ when the cyclic voltammogram is recorded in acetonitrile. Couple IV′ is absent in the cyclic voltammogram when dimethylformamide is used as solvent [Fig. 3(*b*)] or when an excess of a strong ligand such as pyridine is added to the acetonitrile solution. Presumably, when acetonitrile is used as solvent the excess of acetonitrile present would suppress the dissociation of MeCN from [Ni(qtpy)(MeCN)$_2$]$^+$. We propose couple IV′ to be the reduction of undissociated or partially dissociated nickel complex such as [Ni(qtpy)(MeCN)$_2$]$^+$ or [Ni(qtpy)(MeCN)]$^+$. The reduction wave at -1.98 V (III′) can be assigned as the [Ni(qtpy)]–[Ni(qtpy)]$^-$ couple. The fact that couple III′ is more reversible than wave III in the cobalt complex suggests that [Ni(qtpy)]$^-$ is more stable than [Co(qtpy)]$^-$.

Electrodeposition of Cobalt Complex on a Glassy Carbon Electrode.—When the bulk concentration of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ is increased to greater than about 0.2 mmol dm^{-3}, the cyclic voltammogram of the complex (Fig. 4) exhibits an intense irreversible cathodic peak at -1.65 V and a sharp anodic peak at the position of the oxidative wave of couple II. This phenomenon is most pronounced at high complex concentration and is typical of an electrodeposition–redissolution process. At a bulk concentration of 1.0 mmol dm^{-3} of the cobalt complex, integration of the area under the cathodic electrodeposition peak at -1.65 V in the cyclic voltammogram indicates 5.8×10^{-5} C has been consumed which is equivalent to a coverage of *ca.* 7.1×10^{-9} mol cm^{-2} (area of electrode = 0.085 cm^2). From the known dimensions of the complex[15] a monolayer coverage is about 1.6×10^{-10} mol cm^{-2}. Therefore multilayer deposition has occurred on the electrode. Controlled-potential electrolysis of the solution at -1.65 V leads to the formation of a dark brown, electroactive film on glassy carbon or platinum electrode. The film formation requires the addition of 3 e per mol of [Co(qtpy)(OH$_2$)]$^{2+}$ as established by coulometry. Infrared analysis shows the presence of tetrabutylammonium ion in the film. The result of elemental analysis is consistent with the empirical formula [NBu$_4$]$^+$-[Co(qtpy)]$^-$. The cyclic voltammogram of the modified electrode [Fig. 4(*b*)] in pure supporting electrolyte (0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate in acetonitrile) displays two reversible couples at -0.54 and -0.90 V and one irreversible wave at -1.90 V which resembles that of the cobalt complex in homogeneous solution. The UV/VIS spectrum of a sample prepared by anodic dissolution of the film in water is identical to that of the original cobalt complex. These observations suggest that the basic structure of the initial complex is retained in the film. About 7% of the cobalt complexes are electroactive in the film as evaluated from the ratio of integrated currents (from the cyclic voltammogram of the modified electrode) for the signals in the film and the total charge involved in the preparation of the film.

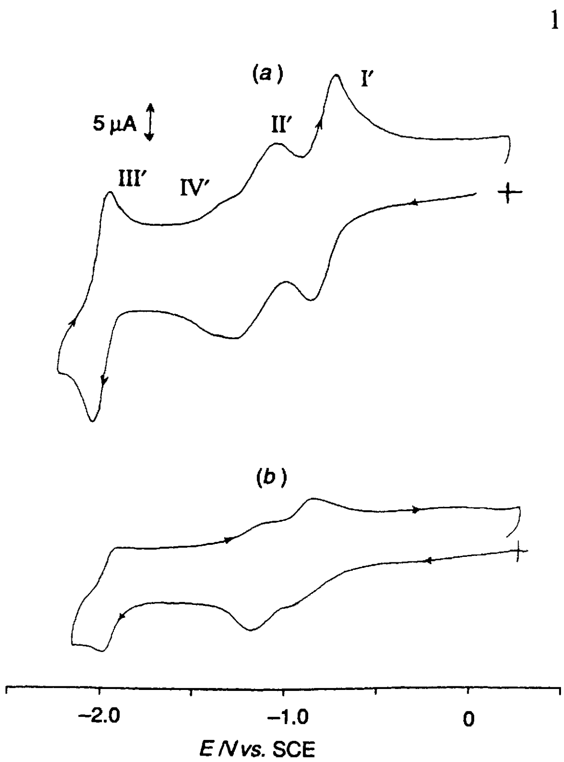

Fig. 3 Cyclic voltammograms of (*a*) 0.15 mmol dm^{-3} [Ni(qtpy)(MeCN)$_2$]$^{2+}$ in acetonitrile and (*b*) 0.1 mmol dm^{-3} [Ni(qtpy)(MeCN)$_2$]$^{2+}$ in dimethylformamide. Other conditions as in Fig. 2

$$\text{Couple I}'\text{: } [\text{Ni(qtpy)(MeCN)}_2]^{2+} + e^- \rightleftharpoons [\text{Ni(qtpy)(MeCN)}_2]^+$$

$$[\text{Ni(qtpy)(MeCN)}_2]^+ \overset{\text{slow}}{\rightleftharpoons} [\text{Ni(qtpy)}]^+ + 2\text{MeCN}$$

$$\text{Couple II}'\text{: } [\text{Ni(qtpy)}]^+ + e^- \rightleftharpoons [\text{Ni(qtpy)}]$$

Scheme 2

For [Ni(qtpy)(MeCN)$_2$]$^{2+}$, no peak attributable to electrodeposition of the nickel complex can be observed even when the complex bulk concentration is greater than about 0.5 mmol dm^{-3}. Controlled-potential electrolysis at -1.55 V did not lead to the formation of a film on the electrode surface visible to the naked eyes.

Electrocatalytic Reduction of Carbon Dioxide.—In the presence of CO$_2$, the cyclic voltammograms of both [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ and [Ni(qtpy)(MeCN)$_2$]$^{2+}$ display a catalytic current at *ca.* -1.95 V corresponding to the reduction peaks III and III′ (Fig. 5). This catalytic current peak is not of particular interest because the potential is too close to the background value where CO$_2$ can be reduced without any metal catalyst. Moreover, even the free quaterpyridine ligand shows a catalytic current in the presence of CO$_2$ at this potential. Perhaps the most intriguing feature in the cyclic voltammograms of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ and [Ni(qtpy)(MeCN)$_2$]$^{2+}$ is that the catalytic current commences at a potential much more anodic (at *ca.* -1.70 V) than that required for the generation of waves III and III′. Constant-potential electrolysis of a 0.2–0.4 mmol

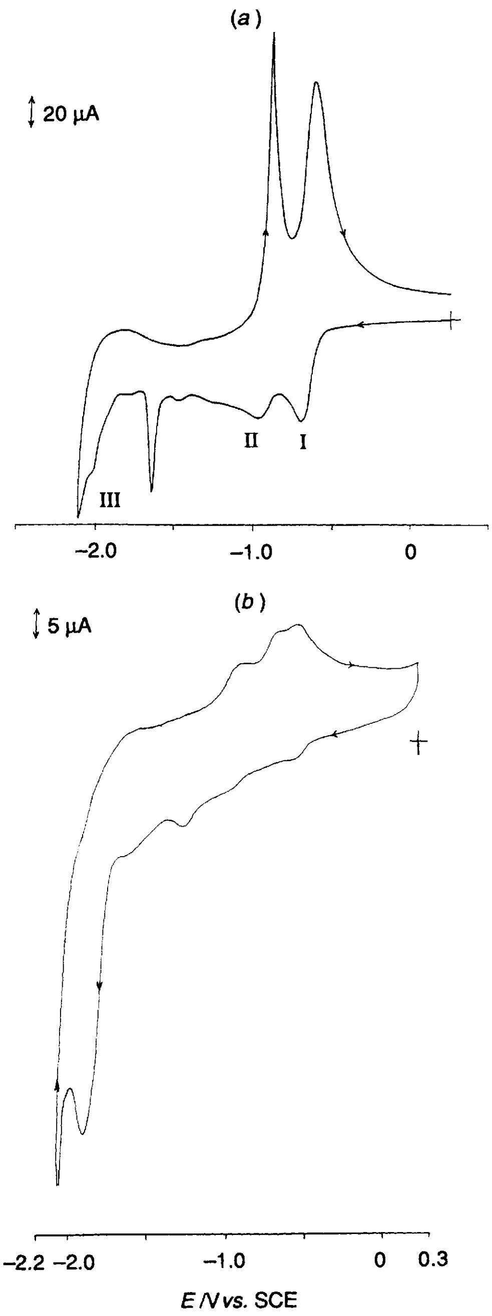

Fig. 4 Cyclic voltammograms of (*a*) 1.0 mmol dm^{-3} [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ showing electrodeposition of the complex on the electrode and (*b*) modified electrode with the deposited film in pure supporting electrolyte

dm^{-3} solution of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ in the presence of CO$_2$ at −1.70 V for 60 min leads to the production of CO with a current efficiency of *ca.* 80% and catalyst turnover (based on the total amount of complex present in solution) of about 20 cycles. No formate or oxalate could be detected by spot tests or ion chromatography. The catalytic current slowly decays upon prolonged electrolysis with the appearance of some light brown precipitates in the solution. These brown precipitates could be due to the formation of insoluble cobalt carbonate complex which deactivates the catalyst. For [Ni(qtpy)(MeCN)$_2$]$^{2+}$ the catalytic current at −1.7 V during controlled-potential electrolysis is much smaller than that of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ even though a trace quantity of CO could be detected after the electrolysis.

It is tempting to attribute the catalytic current at −1.70 V to metal complexes adsorbed/deposited on the electrode surface. Plotting the catalytic current at −1.70 V as a function of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ concentration shows that it is only weakly dependent on the catalyst concentration (Fig. 6). This is consistent with a model that adsorbed complexes are active in the catalytic reduction of CO$_2$. A modified electrode, prepared by holding the potential at −1.65 V for 5 min in a cobalt complex solution, when transferred to a pure supporting electrolyte saturated with CO$_2$ shows in its cyclic voltammogram a catalytic current at *ca.* −1.7 V (Fig. 7). A graphite cloth with deposited cobalt complexes, when transferred to a CO$_2$-saturated supporting electrolyte solution and electrolysis was carried out at −1.7 V for 30 min, produced CO with a current efficiency of about 35%. This demonstrated that cobalt complexes deposited on the electrode surface are responsible for the catalytic activity. The fact that the nickel complex shows much smaller catalytic activity can be attributed to much less nickel complex being adsorbed on the electrode surface.

Similar experiments in aqueous solution (0.1 mol dm^{-3} LiClO$_4$) show that the cobalt-modified electrode is also an

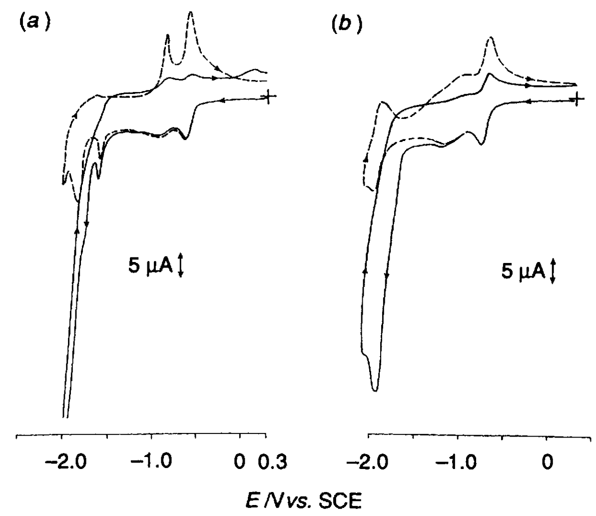

Fig. 5 Cyclic voltammograms of *ca.* 0.6 mm [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ (*a*) and [Ni(qtpy)(MeCN)$_2$]$^{2+}$ (*b*) in acetonitrile under N$_2$ (- - - - -) and under CO$_2$ (———). Working electrode: glassy carbon (area 0.086 cm^2). Scan rate: 100 mV s^{-1}. Supporting electrolyte: 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate

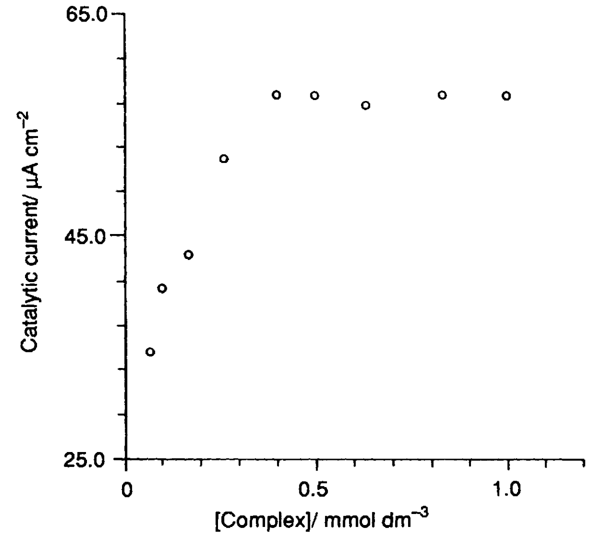

Fig. 6 Plot of the catalytic current at −1.70 V as a function of [Co(qtpy)(OH$_2$)$_2$]$^{2+}$ concentration in the cyclic voltammogram recorded in acetonitrile under CO$_2$

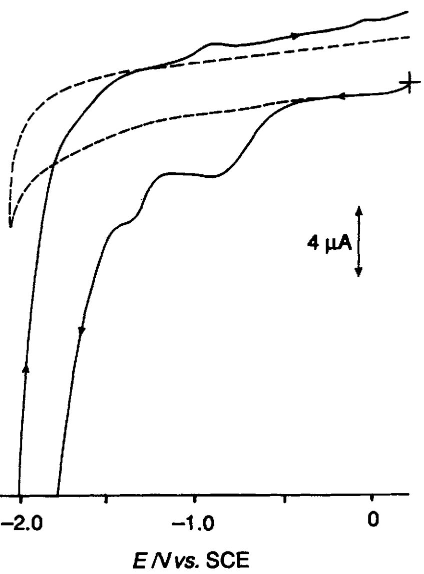

Fig. 7 Cyclic voltammogram of a glassy carbon electrode in pure supporting electrolyte (0.1 mol dm^{-3} NBu_4PF_6 in MeCN) saturated with CO_2 before (- - - -) and after (———) modification with cobalt complex. The electrode was coated by holding the potential at −1.65 V in a 0.6 mmol dm^{-3} solution of $[Co(qtpy)(OH_2)_2]^{2+}$ for 30 min

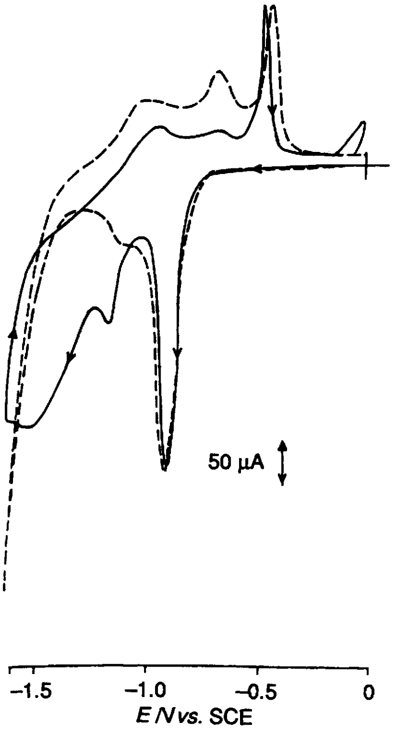

Fig. 8 Cyclic voltammogram of the cobalt-modified electrode in 0.1 mol dm^{-3} $LiClO_4$–water under N_2 (----) and under CO_2 (———). The modified electrode was prepared as in Fig. 7. Scan rate 100 mV s^{-1}

effective catalyst for reduction of CO_2 into CO in water. Fig. 8 shows the cyclic voltammogram under N_2 and CO_2 of the film in an aqueous medium. Bubbling CO_2 induces a strong increase of the cathodic current. Electrolysis at −1.3 V on a graphite cloth coated with [Co(qtpy)] produces CO with a current efficiency of 36% after 20 C have been consumed. Hydrogen gas was produced simultaneously and accounted for the remaining 64% of the current. The catalytic current dropped to 16% of its initial value at the end of the electrolysis.

Conclusion

We have demonstrated that cobalt quaterpyridine complex can be electrodeposited on an electrode surface and that the resulting modified electrode is catalytically active towards the electrochemical reduction of CO_2 to CO both in aqueous and non-aqueous media. The formation of a film on the electrode surface is probably facilitated by the planar and aromatic nature of the co-ordinated quaterpyridine. Research on the catalytic properties of other transition-metal complexes of quaterpyridine is in progress in our laboratories.

Acknowledgements

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