Industrie, and Degussa (loan of K_2PtCl_4). We thank G. Trötscher and H. Hillebrecht for experimental assistance.

Registry No. **1a**, 83350-97-4; **1b**, 113705-71-8; **1c**, 113705-74-1; **2a**, 74539-69-8; **2b**, 113705-76-3; **3**, 113705-50-3; **4a**, 113705-51-4; **4b**, 113705-53-6; **5a**, 113705-55-8; **6**, 113705-57-0; **7**, 113705-59-2; **8**, 113705-61-6; **9**, 113705-62-7; **10**, 113705-64-9; **11a**, 113705-66-1; **11b**, 113705-68-3; **12**, 113705-70-7; **13**, 85886-74-4; **13a**, 92220-61-6; **13b**, 113705-77-4; $[(NH_3)_2Pt(1\text{-}MeU)_2Pt(en)]^{4+}$, 113705-78-5; $[(en)Pt(1\text{-}MeU)_2Pt(en)]^{4+}$, 113725-93-2; $[(en)Pt(1\text{-}MeU)_2Pt(NH_3)_2]^{4+}$, 113705-79-6; $[(NH_3)_2Pt(1\text{-}MeU)_2Pt(bpy)]^{4+}$, 113705-80-9; $[(bpy)Pt(1\text{-}MeU)_2Pt(bpy)]^{4+}$, 113705-85-4; $[(en)Pt(1\text{-}MeU)_2Pt(NH_3)_2]_2^{5+}$, 113705-82-1; $[(NH_3)_2Pt(1\text{-}MeU)_2Pt(bpy)]_2^{5+}$, 113705-83-2; $[(bpy)Pt(1\text{-}MeU)_2Pt(bpy)]_2^{5+}$, 113705-84-3; *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1; $Pt(en)Cl_2$, 14096-51-6; $Pt(bpy)Cl_2$, 13965-31-6; $Pd(en)Cl_2$, 15020-99-2; $Pd(bpy)Cl_2$, 14871-92-2; $[Pd(bpy)(H_2O)_2](NO_3)_2$, 113705-73-0; $[Pd(en)(H_2O)_2]SO_4$, 113705-75-2; $[Pt(NH_3)_2(H_2O)_2](NO_3)_2$, 52241-26-6; $[Pt(en)_2(H_2O)_2](ClO_4)_2$, 33728-67-5; $[Pt(en)_2(H_2O)_2](NO_3)_2$, 52241-27-7; $[Pt(bpy)_2(H_2O)_2](NO_3)_2$, 64800-95-9; $[Pt(bpy)_2(H_2O)_2](ClO_4)_2$, 54822-53-6; $[Pd(en)(H_2O)_2](NO_3)_2$, 62418-53-5; $[(NH_3)_2Pt(1\text{-}MeU)_2Pd(1\text{-}MeU)_2Pt(NH_3)_2]^{3+}$, 113705-81-0.

Supplementary Material Available: Listings of positional and thermal parameters for **4a** and ^1H NMR shifts of mono- and dinuclear complexes, Raman spectra of **8** and **9**, and sections of IR spectra of 1-MeUH, **1a**, **13**, and **4a** (10 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Institut de Chimie, 1, rue Blaise Pascal, F-67000 Strasbourg, France

Electrocatalytic Properties of $Ni(cyclam)^{2+}$ and $Ni_2(biscyclam)^{4+}$ with Respect to CO_2 and H_2O Reduction

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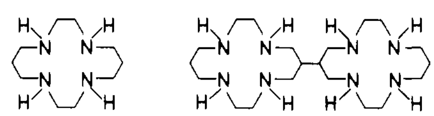
The electrocatalytic abilities of $Ni(cyclam)^{2+}$ and $Ni_2(biscyclam)^{4+}$ have been studied and compared for CO_2 or H_2O reduction. The dimetallic complex is a better electrocatalyst than its mononuclear analogue for evolving H_2 from water. On the other hand, both compounds display analogous properties with respect to CO_2 electroreduction, leading only to C_1 products. In water, CO is the sole reduction product obtained notwithstanding the electrocatalyst used. If low water content DMF is used as a solvent, high faradaic yields of $HCOO^-$ are observed (up to 75%) in addition to CO.

Introduction

Cyclam **1** (1,4,8,11-tetraazacyclotetradecane) displays a very rich coordination chemistry with a large variety of transition metals.[1] In particular, the nickel(II) complex shows a surprising thermodynamic and kinetic stability,[2] which allows its use in a number of catalytic reactions, sometimes under severe conditions. Recent examples include CO_2 electroreduction to CO,[3,4] electrochemical reduction of NO_2^- or NO_3^-,[5] cathodic coupling of alkyl bromides,[6] and epoxidation of olefins.[7] Other related macrocyclic complexes have also been used in electrocatalytic reduction of CO_2.[8] A recent report describes the synthesis of a biscyclam ligand **2** (6,6′-Bi-1,4,8,11-tetraazacyclotetradecane) and its dimetallic complexes[9a] of copper(II) and nickel(II): $Cu_2(\mathbf{2})^{4+}$, $CuNi(\mathbf{2})^{4+}$ and $Ni_2(\mathbf{2})^{4+}$. Until now the dinickel complex has been used as neither a catalyst nor an electrocatalyst.

This article reports the electrocatalytic properties of $Ni_2(\mathbf{2})^{4+}$ with respect to CO_2 or H_2O reduction, with particular emphasis on the comparison between the properties of the mononuclear complex $Ni(\mathbf{1})^{2+}$ and the dimetallic compound $Ni_2(\mathbf{2})^{4+}$. $Ni_2(\mathbf{2})^{4+}$



cyclam **1** biscyclam **2**

possesses two coordination sites that might both be close enough to interact simultaneously with small molecules or their reduction products, leading to potentially different reaction pathways than $Ni(\mathbf{1})^{2+}$ itself. For instance, the reacting centers of the same molecule could bind to two substrates that would react independently from one another or react in a concerted manner. In the latter case, the reaction products might be different from those obtained by using $Ni(\mathbf{1})^{2+}$. As far as CO_2 activation is concerned, an important goal is to favor coupling reactions, leading to C_2 compounds.[10] A general idea is that if two transition-metal centers can be reduced and further react with CO_2 simultaneously, the reduction intermediates obtained from two molecules of CO_2 might form a C-C bond.

Experimental Section

Materials. All products were of reagent grade and were used as received. Acetonitrile (Merck for spectroscopy) and dimethylformamide (DMF) were used without purification. Low water content DMF required for oxalate analysis was obtained by drying commercial grade DMF (Prolabo) overnight over P_2O_5 and distilling under vacuum. The ligand biscyclam (**2**) was obtained by reduction of the bisdioxocyclam[9b] with B_2H_6 as reported previously.[9a] ^1H NMR and mass spectra were as

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Table I. Electrochemical Properties of $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ in Water and in CH_3CN on a GC or Hg Electrode

complex	*E*, V vs SCE (ΔE_p, mV)[a] III/II	II/I	electrode	solvent
$Ni(cyclam)^{2+}$	0.99 (60)	−1.43 (60)	GC	CH_3CN
		−1.47 (70)	HME	CH_3CN
	0.68 (60)	−1.58 (60)	GC	H_2O
		−1.58 (60)	HME	H_2O
$Ni_2(biscyclam)^{4+}$	1.00 (100)	−1.42 (130)	GC	CH_3CN
		−1.44 (140)	HME	CH_3CN
	0.72 (100)[c]	−1.55 (80)[b]	GC	H_2O
		−1.55 (70)[b]	HME	H_2O

[a] $E_{1/2}$ values determined by cyclic voltammetry. Experimental conditions: scan rate = 100 mV s^{-1}; 20 °C; support electrolyte, $NaClO_4$ (0.1 M) in water or tetrabutylammonium perchlorate (0.1 M) in CH_3CN; hanging mercury electrode (HME) or glassy carbon (GC) electrode. [b] pH 12. [c] pH 1.

expected. The complex $Ni_2(\mathbf{2})(BF_4)_4{\cdot}2H_2O$ was prepared in a manner similar to that used for $Ni(\mathbf{1})(BF_4)_2$.[4] It was characterized by elemental analysis (C, H, N, Ni) and by electron spectroscopy (λ_{max} = 450 nm in water, ϵ = 68 M^{-1} cm^{-1}).

Analytical Methods and Procedures. Analytical methods and electrochemical procedures have been previously described.[4] Formic acid was determined by a colorimetric method[11] and by HPLC (Waters).

Results and Discussion

As will be discussed below, the electrocatalytic behavior of $Ni_2(\mathbf{2})^{4+}$ is not markedly different from that of $Ni(\mathbf{1})^{2+}$ with respect to CO_2 reduction: no coupling product could be obtained under the experimental conditions described in the present article. However, both electrocatalysts display significantly different properties with regard to H_2O reduction, the greater reactivity of $Ni_2(\mathbf{2})^{4+}$ as compared to its monometallic analogue being possibly due to a dinuclear effect.

(a) Electrochemical Behavior of $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ in H_2O and in CH_3CN in the Absence of CO_2. Cyclic voltammograms clearly show that the dimetallic complex $Ni_2(\mathbf{2})^{4+}$ can be oxidized or reduced to $Ni_2(\mathbf{2})^{6+}$ or $Ni_2(\mathbf{2})^{2+}$, respectively, at potential values very close to those corresponding to the mononuclear species $Ni(\mathbf{1})^{2+}$ for the $Ni^{III/II}$ and $Ni^{II/I}$ couples. In addition, peak intensities of oxidation and reduction indicate that two electrons are exchanged in each process.

Table I contains the redox potentials of the various electrochemical processes observed for $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ in H_2O or CH_3CN and on either mercury or glassy carbon (GC).

Although the two nickel atoms of $Ni_2(\mathbf{2})^{4+}$ are relatively close to one another (estimated distance ~5–8 Å on CPK models) the two metal centers seem to be electrochemically independent. Contrary to related complexes showing two monoelectronic waves at distinct potentials,[12] the cyclic voltammogram of $Ni_2(\mathbf{2})^{4+}$ shows only two-electron processes. However, the peak to peak separation between the oxidation and reduction reactions are noticeably larger for $Ni_2(\mathbf{2})^{4+}$ than for $Ni(\mathbf{1})^{2+}$, either for the $Ni^{III/II}$ couple or for Ni^{II}/Ni^{I}.

The Ni^{I}/Ni^{0} couple could not be observed for the mononuclear complex in CH_3CN. However, an irreversible and dielectronic wave is clearly seen for $Ni_2(\mathbf{2})^{2+} \rightarrow Ni_2(\mathbf{2})^{0}$, at −1.8 V vs SCE. This wave is not perfectly reproducible, and repeated scans indicate a modification of the surface state of the electrode. It is likely that this phenomenon can be assigned to formation of nickel metal.

Another important difference between $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ rests on the more pronounced reversible character of the redox processes involving the monometallic complex. In aqueous medium and at neutral pH, the Ni^{III}/Ni^{II} and $Ni^{II/I}$ couples of $Ni(\mathbf{1})^{2+}$ are always reversible at a scan rate of 100 mV/s. Under identical conditions, the corresponding couples of $Ni_2(\mathbf{2})^{4+}$ appear to be irreversible. As indicated in Table I, the redox potentials of those couples could only be obtained under extreme acid–base conditions.

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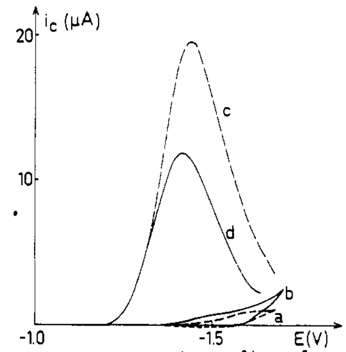


Figure 1. Cyclic voltammograms of $Ni(\mathbf{1})^{2+}$ (10^{-3} M; dashed lines) and $Ni_2(\mathbf{2})^{4+}$ (10^{-3} M; full lines) in 0.1 M $NaClO_4$ under argon (curves a and b) or CO_2 (curves c and d). Conditions: hanging mercury electrode; scan rate 100 mV s^{-1}. For clarity, reverse scans of curves c and d (under CO_2) have been omitted.

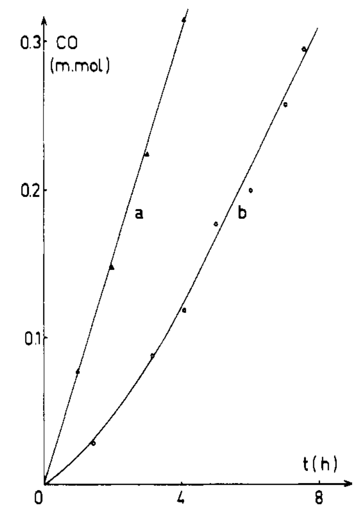


Figure 2. Amount of CO produced as a function of time electrolysis (−1.25 V vs SCE; Hg cathode) in water (0.1 M $NaClO_4$) at room temperature: (a) $Ni(\mathbf{1})^{2+}$ (4 × 10^{-4} M); (b) $Ni_2(\mathbf{2})^{4+}$ (1.5 × 10^{-4} M).

In order to stabilize the trivalent state of nickel, acidic medium was used ($2Ni^{III}/2Ni^{II}$) whereas base was added for studying the $2Ni^{II}/2Ni^{I}$ couple.

(b) Electrocatalytic Reduction of CO_2 to CO by $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ in an Aqueous Medium. It has recently been shown that $Ni(\mathbf{1})^{2+}$ displays unusual electrocatalytic properties for reducing CO_2 to CO at −1.0 V vs NHE in aqueous medium.[3] The process is very efficient, and the selectivity of reduction of CO_2 versus that of H_2O is surprisingly high.[4] In Figure 1 are represented the cyclic voltammograms of the two complexes studied in water, either under CO_2 or under argon. Clearly, $Ni_2(\mathbf{2})^{4+}$ seems to be less efficient an electrocatalyst of CO_2 reduction than $Ni(\mathbf{1})^{2+}$: the catalytic current obtained with the former complex is only about half that observed with $Ni(\mathbf{1})^{2+}$.

Electrolysis at fixed potential has been performed by using both complexes under identical conditions. The results obtained in a typical experiment (at −1.25 V vs SCE) are shown in Figure 2. The amount of CO produced in the course of this particular experiment is roughly three times larger with $Ni(\mathbf{1})^{2+}$ than with $Ni_2(\mathbf{2})^{4+}$. This observation is in agreement with the ratio of the catalytic peak intensities found for those two complexes (see Figure 1). In each case, the faradaic yield calculated for CO production is almost quantitative (>93%). However, with $Ni_2(\mathbf{2})^{4+}$ as an electrocatalyst, small amounts of H_2 are obtained (~3% of faradaic yield) whereas H_2 is not detected with $Ni(\mathbf{1})^{2+}$. We shall come back later to this important point.

Although at the present stage it is not clear why $Ni(\mathbf{1})^{2+}$ is a few times more efficient than its dimetallic analogue, this difference might tentatively be accounted for by considering the corresponding adsorbed species. The function of those species in the overall electrocatalytic reaction is probably of utmost im-

Table II. Electrochemical Reduction of CO_2 in DMF: Comparison of $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ as Electrocatalysts[a]

E, V vs SCE	electro-catalyst	μmol of CO produced[b]	μmol of $HCOO^-$ produced[b]	$to._{CO}$[c]	$to._{HCOO^-}$[c]	η_{CO}, %	η_{HCOO^-}, %	Q_{CO}, C	Q_{HCOO^-}, C	Q_{tot}, C	electrolysis time, h
−1.5[d]	$Ni(\mathbf{1})^{2+}$									6.6	5
−1.6										1	1
−1.5										1.8	6.67
−1.4	$Ni(\mathbf{1})^{2+}$	15	46	0.99	3.2	24	75	2.8	9.0	12	5
−1.4	$Ni_2(\mathbf{2})^{4+}$	6	24	0.76	3.2	16	68	1.1	4.6	6.8	5
−1.5	$Ni(\mathbf{1})^{2+}$	73	82	4.7	5.3	49	52	14.1	15.0	28.6	5
−1.5	$Ni_2(\mathbf{2})^{4+}$	15	40	1.9	5.1	24	48	2.9	7.8	16.2	5.67
−1.6	$Ni(\mathbf{1})^{2+}$	186	139	12.2	9.1	55	41	35.8	26.7	65.1	6.67
−1.6	$Ni_2(\mathbf{2})^{4+}$	116	67	15.4	9.0	65	38	22.3	13.0	34.0	6

[a] Experimental conditions: 75 mL of DMF; $[NaClO_4]$ = 0.1 M; 20 °C, 1 atm of CO_2; mercury cathode. In each experiment the nickel concentration is 2.00×10^{-4} M. [b] The detection limit is estimated as 2 μmol for CO and 7 μmol for $HCOO^-$. [c] $to._{CO}$ and $to._{HCOO^-}$ are the overall turnover numbers on the electrocatalyst respectively for CO and $HCOO^-$. [d] In this run, 14.8 μmol of H_2 are produced with 43% of faradaic efficiency.

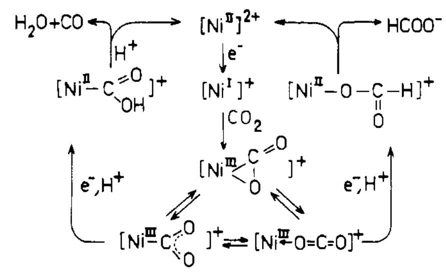
portance.[4] If one supposes that only one nickel center of $Ni_2(\mathbf{2})^{4+}$ is directly involved in each reaction cycle and if one takes into account the larger surface area of $Ni_2(\mathbf{2})^{4+}$ as compared to $Ni(\mathbf{1})^{2+}$ (assuming an adsorption phenomenon involving the ligand plane and a complete electrode surface coverage), it is expected that the superficial density of active sites is smaller with $Ni_2(\mathbf{2})^{4+}$ than with $Ni(\mathbf{1})^{2+}$.

(c) Electrocatalytic Reduction of CO_2 to $HCOO^-$ and CO in DMF, in the Presence of $Ni(\mathbf{1})^{2+}$ or $Ni_2(\mathbf{2})^{4+}$. Cyclic voltammograms performed under CO_2 in DMF show, for both complexes, a significant increase of the cathodic current below −1.3 V as compared to the same system under N_2. At the same time, the reoxidation peak ($Ni^{I} \rightarrow Ni^{II}$) is no longer detected whereas the redox process is reversible under nitrogen. However, the effect is much less pronounced in DMF than in aqueous medium. In addition, no shift of the reduction peak toward less negative potentials is observed under CO_2. Electrolyses have been carried out at various potentials (−1.4, −1.5, and −1.6 V vs SCE). Quantitative analysis of the reduction products show that only formate and CO are obtained. Some representative data are collected in Table II. Blank experiments clearly demonstrate that no CO nor $HCOO^-$ is produced if either the nickel complex or CO_2 is omitted. In addition, the process is catalytic with respect to $Ni(\mathbf{1})^{2+}$ or $Ni_2(\mathbf{2})^{4+}$ since overall turnover numbers of up to 25 were obtained. H_2 could not be detected as a reduction product. This is not surprising if one takes into account (i) the exceptional selectivity of $Ni(\mathbf{1})^{2+}$ for electroreducing CO_2 versus H_2O, even in aqueous medium, and (ii) the relatively low water content of the medium presently used (H_2O ~0.2% i.e., $[H_2O]$ ~ 0.1 M).

Much less expected is the formation of $HCOO^-$, this product being even more abundant than CO. Indeed, unmediated systems lead in general to $HCOO^-$ in aqueous medium[13] and to other reduction products in low protic medium,[14] which is exactly the reverse behavior of $Ni(1)^{2+}$ or $Ni_2(2)^{4+}$. Other transition-metal complexes (ruthenium[15-17] or rhenium[18,19]) display analogous electrocatalytic properties in organic medium, also leading to $HCOO^-$ from CO_2. At the present stage, mechanistic considerations concerning the effect of the medium on the course of the reaction are highly speculative. However, it might be argued that proton concentration should have a strong influence on the conversion reaction of a nickel–carboxylate intermediate (Ni–COOH) to a nickel carbonyl (Ni–CO).

On the other hand, the formation of nickel(II) formate from the same nickel–carboxylate species or from a side-on CO_2 complex could be involved in the course of $HCOO^-$ formation, this same reaction being apparently unfavored in acidic medium. A tentative reaction scheme is given in Scheme I. From the electrochemical data of Table II, it is clear that for both complexes $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ the intensity of the catalytic current increases as the applied potential is more negative, and more interestingly, the proportion of $HCOO^-$ versus CO is higher at less negative potentials. A possible explanation could be that the nickel(II) formate species (Ni^{II}–OOC–H) are electrochemically formed more readily than the nickel–carboxylate (Ni^{II}–COOH) species.

Scheme I



From the results of Table II, it turns out that the overall faradaic yield (CO + $HCOO^-$) is close to 100% for $Ni(\mathbf{1})^{2+}$ but it might be significantly lower when $Ni_2(\mathbf{2})^{4+}$ is used as electrocatalyst. Another important difference between both catalysts rests on the electrolysis current intensity, which is roughly twice as important for $Ni(\mathbf{1})^{2+}$ than for $Ni_2(\mathbf{2})^{4+}$, under identical conditions. Likewise for CO_2 reduction in aqueous medium, this difference might originate from the larger molecular surface area of the dinuclear complex as compared to $Ni(\mathbf{1})^{2+}$, assuming that only one nickel atom of $Ni_2(\mathbf{2})^{4+}$ is active.

With drastically dried DMF ($[H_2O]$ < 0.01 M), no oxalate could be detected either with $Ni(\mathbf{1})^{2+}$ or with $Ni_2(\mathbf{2})^{4+}$ as electrocatalyst. Clearly, $Ni_2(\mathbf{2})^{4+}$ does not favor formation of C_2 products as compared to $Ni(\mathbf{1})^{2+}$.

(d) Electrocatalytic Reduction of Water by $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$. The search for new active catalysts able to favor hydrogen evolution from water and an electron source has been extremely active over the past decade. This work is related to the field of chemical storage of light or electrical energy,[20] with a particular emphasis on the light-driven water splitting reaction.[21] Clearly, if this reaction is to be used practically in the future as a means of producing H_2, highly efficient catalytic systems able to induce H_2 (and O_2) formation from water have to be developed. They may be either homogeneous or suspended species in photochemical devices or confined to an electrode surface in photoelectrochemical cells.

Until now, only a limited number of purely molecular systems (as opposed to metal or metal oxide heterogeneous catalysts) have been proposed,[22-25] due to the difficulty inherent to the dielectronic

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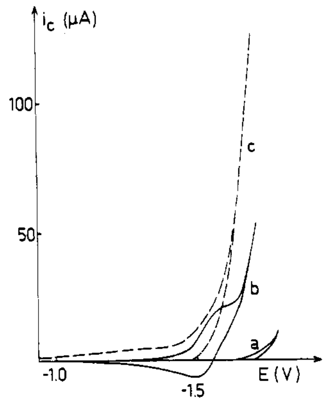


Figure 3. Cyclic voltammograms (on Hg), in water (0.1 M $NaClO_4$; pH 7.4) under argon (scan rate 100 mV s^{-1}): (a) supporting electrolyte; (b) $Ni(\mathbf{1})^{2+}$ (2×10^{-3} M); (c) $Ni_2(\mathbf{2})^{4+}$ (10^{-3} M).

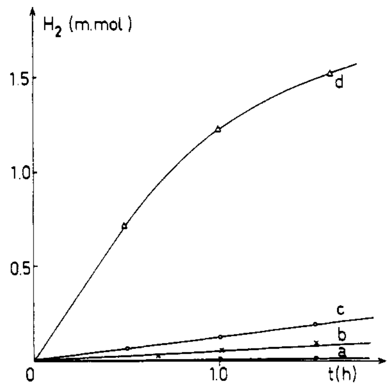


Figure 4. Amount of H_2 produced in the course of an electrolysis in H_2O at pH 7 (phosphate buffer, 0.2 M): (a) without any added complex; (b) in the presence of $Ni(BF_4)_2$ (2.3×10^{-4} M); (c) with $Ni(\mathbf{1})^{2+}$ (2×10^{-4} M); (d) with $Ni_2(\mathbf{2})^{4+}$ (10^{-4} M). Conditions: room temperature; Hg pool; applied potential = −1.5 V vs SCE.

nature of the reaction ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$). Although the overvoltage for reducing H_2O to H_2 remains relatively important in the presence of $Ni(\mathbf{1})^{2+}$ or its dimetallic analogue, as shown by the CV's given in Figure 3, a significant catalytic effect can be detected, in particular for $Ni_2(\mathbf{2})^{4+}$. At pH 7.4, the $Ni(\mathbf{1})^{2+/+}$ couple is reversible under argon, proton reduction becoming effective only 80 mV below the Ni^{II} reduction peak potential (−1.57 V) whereas the $Ni_2(\mathbf{2})^{4+/2+}$ couple is totally irreversible. For the latter a very intense catalytic current is measured at the reduction peak potential observed in basic medium for the $2Ni^{II}/2Ni^{I}$ couple (see paragraph a). This catalytic effect and the different behaviors of $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ have been confirmed by coulometric experiments at fixed potential ($E = -1.5$ V vs SCE) in various media. The most representative data are given in Figure 4 and Figure 5. Without catalyst, only trace amounts of H_2 are obtained (Figure 4, curve a). In the presence of $Ni(BF_4)_2$, small quantities of H_2 are detected, the obtention of which is probably due to the formation of nickel amalgam, this species acting as a catalyst (Figure 4, curve b).

Turnover numbers of up to 100 on the nickel complexes could be reached, clearly showing the electrocatalytic nature of the process. In addition, UV–visible spectroscopy measurements performed at the end of electrolysis indicate that neither $Ni(\mathbf{1})^{2+}$ nor $Ni_2(\mathbf{2})^{4+}$ are damaged in the course of the electrochemical reaction.

As for electrochemical reduction of CO_2 in an aqueous medium,[4] the participation of adsorbed species acting as catalyst at the Hg surface seems to be important. Indeed, the electrocatalyst concentration has only a minor effect on the efficiency of H_2 production, as indicated by the plateau shape of the curves shown in Figure 6.

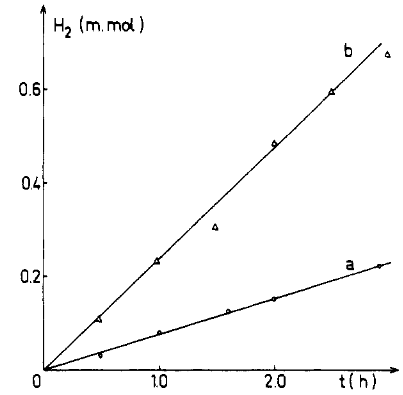


Figure 5. Same experiment as in Figure 4 except that the electrolysis took place at pH 8 (phosphate buffer, 0.2 M): (a) $Ni(\mathbf{1})^{2+}$; (b) $Ni_2(\mathbf{2})^{4+}$.

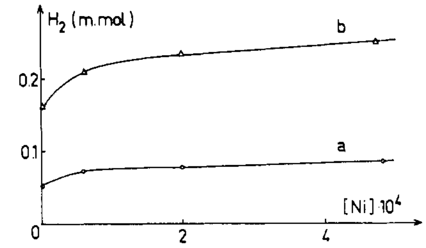
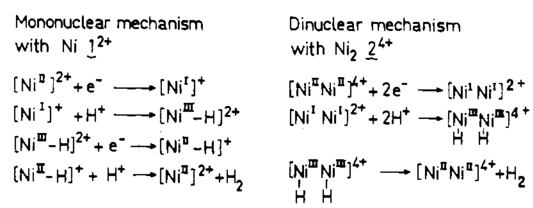


Figure 6. Production of H_2 by 1 h of electrolysis as a function of analytical nickel concentration at 20 °C: (a) $Ni(\mathbf{1})^{2+}$; (b) $Ni(\mathbf{2})^{4+}$. Conditions: phosphate buffer (0.2 M) at pH 8; Hg cathode; applied potential = −1.5 V vs SCE.

Scheme II



It is intriguing that the efficiency of $Ni_2(\mathbf{2})^{4+}$ as an electrocatalyst of H_2O reduction to H_2 is significantly larger than that of $Ni(\mathbf{1})^{2+}$, the analytical nickel concentration being the same. This behavior is noticeably different from that regarding CO_2 electroreduction. Depending on the pH, $Ni_2(\mathbf{2})^{4+}$ is three (at pH 8) to 10 (at pH 7) times more active than $Ni(\mathbf{1})^{2+}$. These results tend to indicate that the dinuclear nature of $Ni_2(\mathbf{2})^{4+}$ increases its efficiency as compared to $Ni(\mathbf{1})^{2+}$. In other words, the short distance between the two nickel atoms of $Ni_2(\mathbf{2})^{4+}$ might lead to some cooperativity, the electrochemical reaction occurring on one site being favored by the second site. A reaction mechanism involving a dihydride intermediate might account for this observation, a possible reaction scheme being indicated in Scheme II.

Conclusion

The results of the present study stress several important points concerning CO_2 or water reduction by nickel complexes.

(i) Both $Ni(\mathbf{1})^{2+}$ and $Ni_2(\mathbf{2})^{4+}$ are exceptionally selective electrocatalyst for reducing CO_2 in aqueous medium, no other reduction product than CO being formed. In anhydrous medium, the catalytic properties of the complexes are very different from those in water. In low water content DMF ($[H_2O] < 0.2\%$), formate is obtained preferentially to CO, faradaic yields of up to 75% of $HCOO^-$ being observed. This apparently paradoxical behavior may be related to the formation of nickel formate or nickel carboxylate, depending on the experimental conditions.

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(ii) As far as CO_2 electroreduction is concerned, $Ni_2(\mathbf{2})^{4+}$ shows no particular properties as compared to $Ni(\mathbf{1})^{2+}$. In particular, it does not lead to coupling reactions.

(iii) On the other hand, the electroreduction of water is markedly more efficiently catalyzed by the dinuclear complex than by $Ni(\mathbf{1})^{2+}$. The involvement of dihydride intermediates of the type Ni(H)-Ni(H) might account for this result.

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Registry No. $Ni(\mathbf{1})^{2+}$, 46365-93-9; $Ni_2(\mathbf{2})^{4+}$, 102649-30-9; DMF, 68-12-2; CO_2, 124-38-9; H_2O, 7732-18-5; H_2, 1333-74-0; CO, 630-08-0; $HCOO^-$, 71-47-6; Hg, 7439-97-6; C, 7440-44-0.

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Utility of Cyclodichlorophosphazene as a NaC_5H_5 Scavenging Reagent: Synthesis of an Organoyttrium Hydroxide Complex and the X-ray Crystal Structure of the Layered Compound $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$

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$(C_5H_5)_3Y(THF)$ reacts with NaOH in THF to form NaC_5H_5 and $(C_5H_5)_2Y(OH)(THF)$. Treatment of the mixture of solids from this reaction with an 80%:20% mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ in toluene allows the separation of the hydroxide complex by filtration. $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$, formed by partial hydrolysis of a $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)/C_6H_5C{\equiv}CC_6H_5$ mixture, crystallizes from a 1:2 mixture of THF/hexane in the presence of $C_6H_5C{\equiv}CC_6H_5$ in space group $P2_1/c$ with unit cell dimensions $a = 9.346$ (7) Å, $b = 21.284$ (8) Å, $c = 8.262$ (5) Å, $\beta = 112.50$ (3)°, and $Z = 2$ for $D_{calcd} = 1.43$ g cm^{-3}. Least-squares refinement on the basis of 513 observed reflections converged to a final $R = 0.068$. The molecular structure consists of two $(C_5H_5)_2Y$ units bridged by OH groups with Y-O distances of 2.33 (2) and 2.36 (2) Å. The $C_6H_5C{\equiv}CC_6H_5$ molecules occupy alternate layers between layers of the hydroxide molecules. The layers are oriented such that the hydroxide ligands are oriented toward the C≡C bonds of the diphenylethyne molecules.

Introduction

Hydrolysis is a common mode of decomposition for the organometallic complexes of yttrium and the f elements, and hydroxide complexes are usually assumed to be the products.[2-4] Despite the apparent prevalence of hydroxide complexes in these reactions and the presumed existence of intermediates containing both organometallic ligands and hydroxide ligands, no structural evidence has previously been presented on organometallic hydroxide yttrium or f element species.[5] We recently were able to isolate crystals of an organometallic yttrium hydroxide complex cocrystallized with $C_6H_5C{\equiv}CC_6H_5$, and we report here on the resulting layered structure. In addition, we describe a novel synthesis of $(C_5H_5)_2Y(OH)(THF)$ using a reagent that may have utility in other reactions which form NaC_5H_5 as a byproduct.

Experimental Section

All of the complexes described below are air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted by using Schlenk, vacuum-line, and glovebox (Vacuum/Atmospheres HE-43 Dri Lab) techniques.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were obtained on a Bruker 250-MHz spectrometer. Chemical shifts were assigned relative to C_4D_7HO, 1.79 ppm, for spectra in THF-d_8. Complexometric metal analyses were obtained as previously described.[7]

Materials. Hexane was washed with sulfuric acid, dried over $MgSO_4$, and distilled from sodium benzophenone ketyl solubilized with tetraglyme. Toluene and THF were distilled from sodium benzophenone ketyl. THF-d_8 and benzene-d_6 were vacuum transferred from sodium benzophenone ketyl. NaOH was ground to a fine powder and heated to 120 °C under vacuum. Technical grade $(NPCl_2)_x$ (80% $x = 3$ and 20% $x = 4$; Aldrich) was degassed before use. $(C_5H_5)_3Y(THF)$[8] and $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$[9] were prepared according to the literature.

$(C_5H_5)_2Y(OH)(THF)$. NaOH (9 mg, 0.22 mmol) was suspended in 45 mL of THF containing $(C_5H_5)_3Y(THF)$ (80 mg, 0.22 mmol). The reaction was stirred for 2 days and filtered through a fine frit. The solvent was removed from the filtrate by rotary evaporation, giving a mixture of $(C_5H_5)_2Y(OH)(THF)$ and NaC_5H_5 as a pink powder (50 mg). A solution of $(NPCl_2)_x$ (152 mg, 0.44 mmol) in 25 mL of toluene was added to the pink powder, and the mixture was stirred overnight. The suspension was filtered to give $(C_5H_5)_2Y(OH)(THF)$ (45 mg, 66%), which was pure by ^1H NMR spectroscopy. Anal. Calcd for $YC_{14}H_{19}O_2$: Y, 28.85. Found: Y, 28.0. ^1H NMR (THF-d_8): δ 6.07 (s, C_5H_5). IR (KBr) 3540 m, 3060 s, 2960 s, 2920 m, 2900 m, 1700 m, 1620 m, 1580 m, 1560 m, 1520 m, 1500 m, 1360 w, 1100 s, 1080 s, 1060 s, 1050 s, 770 s cm^{-1}.

$(C_5H_5)_2Y(OH)(THF)$ can be desolvated by heating it to 110 °C overnight under vacuum (10^{-5} Torr). Anal. Calcd for $YC_{10}H_{11}O$: Y, 37.66. Found: Y, 38.7. Only decomposition was observed in attempts to sublime this material at temperatures as high as 300 °C. The desolvate is not soluble in toluene. Addition of THF regenerates $(C_5H_5)_2Y(OH)(THF)$.

$(C_5H_5)_2Y(OH)(THF)$ was also synthesized from $(C_5H_5)_3Y(THF)$ (228 mg, 0.64 mmol) and H_2O (11.5 mL, 0.64 mol). The degassed water in 10 mL of THF was added over 45 min to 40 mL of a solution of $(C_5H_5)_3Y(THF)$ cooled to −78 °C. The reaction was allowed to slowly warm to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was washed several times with toluene. The ^1H NMR spectrum of this product showed it to be a mixture of $(C_5H_5)_2Y(OH)(THF)$ (60% yield) and another THF-soluble product with a C_5H_5 resonance at δ 5.83. Since separation of these two species was not readily accomplished, the synthesis given above is preferable.

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