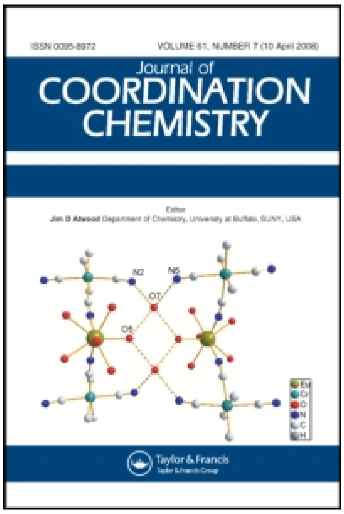

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SYNTHESIS AND CHARACTERIZATION OF DICATIONIC NICKEL COMPLEXES

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Dicationic nickel complexes have been prepared by chemical and electrochemical oxidation of metallic nickel, by methathetical exchange of nickel chloride with halide abstracting agents ($ZnCl_2$, Zn, $AlCl_3$, Al) and by reaction of nickel acetate with strong Brönsted acids (HBF_4, CF_3SO_3H). The resulting complexes were characterized by IR, UV-vis, Rutherford Backscattering Spectroscopy (RBS), and magnetic moment measurements as being octahedral, with six nitrile ligands.

Keywords: nickel complexes; dicationic complexes; synthesis; characterization

INTRODUCTION

We have focused our attention on nickel(II) cationic complexes in which the counter-anion is weakly or non-coordinating and the metal is coordinated by nitrile ligands. These complexes show high activity and selectivity when combined with organoaluminum compounds in C—C bond forming reactions, such as ethylene[1] and propylene[2–3] oligomerization, styrene hydrovinylation[4] and butadiene polymerization.[5] The synthesis of some of these complexes was described previously, either by chemical oxidation of metallic nickel with $NOBF_4$,[6] or by the reaction between nickel chloride and zinc[7] to afford $[Ni(MeCN)_6][BF_4]_2$ and $[Ni(MeCN)_6][ZnCl_4]$, respectively. A general and simple method for the preparation of this class of complexes is desirable.

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In the present article we describe the synthesis of $[Ni(MeCN)_6][BF_4]_2$ by electrochemical oxidation of metallic nickel, or from nickel acetate in the presence of HBF_4. Dicationic complexes with different counter-anions can be obtained by using appropriate Brönsted acids. On the other hand, we have found that the complex $[Ni(MeCN)_6][ZnCl_4]$ can be obtained easily from either reaction with zinc or zinc chloride. In this case, the exchange with other metals allows extension of the counter-anions to new complexes like $[Ni(MeCN)_6][AlCl_4]_2$ and $[Ni(MeCN)_6][CF_3SO_3]_2$. All these syntheses are carried out using nitriles (acetonitrile or benzonitrile) as solvent to afford in very high yields of dicationic nickel complexes containing weakly coordinating solvent molecules.

EXPERIMENTAL

All preparations were performed using standard Schlenk tube techniques under dry argon. Solvents were distilled over drying agents immediately before use. Metallic nickel (Riedel) was treated with diluted hydrochloric acid, washed with water until neutrality was achieved and dried under reduced pressure. Nickel chloride (Vetec), nickel acetate (Aldrich), nitrosonium tetrafluoroborate (Aldrich), zinc (Riedel), zinc chloride (Ecibra), aluminum (Riedel) were dried under vacuum whereas tetrafluoroboric acid (solution 54% in diethyl ether, Merck) and trifluoromethanesulfonic acid (98%, Aldrich) were used without purification. Acetonitrile (Merck) and benzonitrile (Merck) were distilled over P_2O_5 prior to use as solvents.

Preparation of $[Ni(MeCN)_6][BF_4]_2$ (1)

Method A

$[Ni(MeCN)_6][BF_4]_2$ **1** was prepared by oxidation of metallic nickel with $NOBF_4$ in 90% yield as previously described by Hathaway.[6]

Method B

1.68g of $Ni(CH_3COO)_2$ (9.5 mmol) was dissolved in dry acetonitrile (30 mL) and 3.5mL of HBF_4 (20mmol) was added. The mixture was stirred until solubilization of the nickel acetate was achieved. The solution was evaporated and the resulting blue crystals were dried under vacuum. The blue solid was purified by recrystallization from acetonitrile/ether solution and dried under reduced pressure giving 4.00g of **1** (88% yield).

Method C

A nickel wire (Aldrich, 99.99%) and a platinum counter-electrode were immersed in a mixture of 2 mL of tetrafluoroboric acid-diethyl ether complex (54%), and 10 mL of acetonitrile. A 100 mA anodic current was applied to the nickel electrode for 8 h. The resulting blue solution was evaporated and dried under vacuum. The blue solid was purified by recrystallization from acetonitrile/ether solution and dried under vacuum giving 1.78 g of **1**, in a 60% yield based on tetrafluoroboric acid.

Preparation of $[Ni(PhCN)_6][BF_4]_2$ (2)

The complex was prepared similarly to the parent acetonitrile derivative in method A above. 0.5g of metallic nickel (8.56mmol) in 30mL of PhCN were mixed with 1.0g of $NOBF_4$ (8.56mmol). The solution immediately became blue and was filtered. The solvent was removed under reduced pressure and the solid obtained was recrystallized in PhCN, giving 2.99g of **2** (82% yield).

Preparation of $[Ni(MeCN)_6][ZnCl_4]$ (3)

Method D

2.5g of nickel chloride (19.3mmol) and 0.25g metallic zinc (3.8mmol) were dissolved in 10mL of acetonitrile under stirring. The reaction became immediately blue and metallic nickel precipitate. After filtration the solvent was removed under reduced pressure. The blue solid was recrystallized from hot acetonitrile and dried under reduced pressure, giving 1.94g of **3**, in 99% yield based on metallic zinc.

Method E

Another way to obtain **3** is following the same procedure described in method D, but using $ZnCl_2$ (2.6g, 19mmol) as the zinc source. The same product is obtained in 80% yield based on nickel.

Preparation of $[Ni(MeCN)_6][CF_3SO_3]_2$ (4)

Complex **4** was prepared similarly to complex **1** in method B by using CF_3SO_3H instead of HBF_4. $Ni(CH_3COO)_2$ (0.74 g, 4.2 mmol) was dissolved in dry acetonitrile (30 mL) and 1 mL of CF_3SO_3H (11.3 mmol) was added. The mixture was stirred until solubilization of the nickel acetate was achieved. The solution was partially evaporated and the complex was precipitated by ether addition. After filtration, the resulting blue solid was dried under vacuum and purified by recrystallization from acetonitrile/ether solution. The resulting blue solid was dried under reduced pressure giving 1.77 g of **4** (70% yield).

Preparation of $[Ni(MeCN)_6][AlCl_4]_2$ (5)

The complex **5** was prepared similarly to complex **3** in method D by using Al instead of Zn and method E by using $AlCl_3$ instead of $ZnCl_2$.

Method D

Nickel chloride (3.64 g, 28.2 mmol) and 0.53 g of metallic aluminum (19.6 mmol) were dissolved in 20 mL of acetonitrile under stirring. The reaction became immediately blue and metallic nickel precipitate. The solution was filtered and the solvent removed under reduced pressure. The blue solid was recrystallized from hot acetonitrile and dried under reduced pressure, giving 1.94g of 5, in a 40% yield based on metallic aluminum.

Method E

Complex 5 is obtained in 86% yield based on nickel by using $AlCl_3$ (3.75 g, 29.1 mmol) as the aluminum source.

Analytical Techniques

Electronic absorption spectra were recorded using a Shimadzu UV160-A spectrophotometer for $3. \times 10^{-2}$M solutions of the complexes in MeCN or PhCN in 1 cm pathlength cells in the region 200–1100 nm. The IR spectra of the complexes in the region 400–4000 cm^{-1} were recorded with the complexes as Nujol mulls on KBr plates using a Perkin Elmer 1430 spectrometer. Elemental analysis was performed by Rutherford Backscattering Spectroscopy, using the 500 kV-HVEE Ion Implanter of the 'Instituto de Física-UFRGS' with an α-particle energy of 0.8 MeV. The incident and detection angles were 0° and

165° with respect to the incident beam direction. From the analysis of the spectra the elemental atomic ratios in the samples were obtained with a precision of 10%.[8] Magnetic moments of solid samples were measured with a Faraday balance 7600 at room temperature.

RESULTS AND DISCUSSION

The oxidation process can be performed chemically with $NOBF_4$, as described by Hathaway[6] (eq. 1) or alternatively, electrochemically in the presence of HBF_4 (eq. 2). All these procedures lead to **1** with good yields. If these reactions are carried out in the presence of PhCN instead of MeCN, **2** is obtained.

$$\mathrm{Ni} + 2\,\mathrm{NOBF_4} \xrightarrow{\mathrm{RCN}} \begin{array}{l}[\mathrm{Ni(RCN)_6}][\mathrm{BF_4}]_2 + 2\,\mathrm{NO}\\ 1 : \mathrm{R} = \mathrm{Me}\\ 2 : \mathrm{R} = \mathrm{Ph}\end{array} \qquad (1)$$

$$\mathrm{Ni} + 2\,\mathrm{HBF_4} \underset{\text{eletrochem.}}{\xrightarrow{\mathrm{MeCN}}} \underset{1}{[\mathrm{Ni(MeCN)_6}[\mathrm{BF_4}]_2} + \mathrm{H_2} \qquad (2)$$

Nickel chloride can be used in combination with a Lewis acid to produce the dicationic complexes by transfer of the chloride to the main-group metal. This procedure is very simple and consists of mixing nickel chloride with a Lewis acid such as $ZnCl_2$ in acetonitrile for a few minutes (eq. 3). After filtration, solvent evaporation and recrystallization **3** is obtained in 80% yield. The synthesis of **3** described in the literature consists of extracting nickel chloride and zinc dust with hot acetonitrile in the presence of dry sand.[7] On other hand, the use of metallic zinc instead of zinc chloride precludes formation of metallic nickel and enables II synthesis of **3** in 99% yield based on zinc (eq. 4). This procedure can be extended to other Lewis acids like aluminum trichloride (eq. 5) and aluminum (eq. 6).

$$\mathrm{NiCl_2} + \mathrm{ZnCl_2} \xrightarrow{\mathrm{MeCN}} \underset{3}{[\mathrm{Ni(MeCN)_6}][\mathrm{ZnCl_4}]} \qquad (3)$$

$$2\,\mathrm{NiCl_2} + \mathrm{Zn} \xrightarrow{\mathrm{MeCN}} \underset{3}{[\mathrm{Ni(MeCN)_6}][\mathrm{ZnCl_4}]} + \mathrm{Ni} \qquad (4)$$

$$NiCl_2 + 2\,AlCl_3 \xrightarrow{MeCN} \underset{5}{[Ni(MeCN)_6][AlCl_4]_2} \qquad (5)$$

$$4\,NiCl_2 + 2\,Al \xrightarrow{MeCN} \underset{5}{[Ni(MeCN)_6][AlCl_4]_2} + 3\,Ni \qquad (6)$$

A nickel salt with a good leaving group as the acetate ligand reacts immediately with a strong Bronsted acid (eq. 7) like tetrafluoroboric acid to give the complex $[Ni(MeCN)_6][BF_4]_2$ **1** with 88% yield ($X = BF_4^-$). This procedure can be extended to other Bronsted acids, like trifluoromethanesulfonic acid (5; $X = CF_3SO_3^-$) with similar yield.

$$Ni(OAc)_2 + HX \xrightarrow{MeCN} \begin{array}{l} [Ni(MeCN)_6][X]_2 \\ 1 : X = BF_4^- \\ 4 : X = CF_3SO_3^- \end{array} \qquad (7)$$

Characterization of Dicationic Nickel Complexes Containing Nitriles as Ligands

The main IR bands of the nickel complexes in the region 4000–400cm^{-1} are presented in Table I together with their assignment. The dicationic nickel complexes show characteristic nitrile C≡N stretching bands[9] around 2300 cm^{-1}. The vibrations due to the XY_4^- tetrahedral ion are observable in BF_4^- and $AlCl_4^-$ anions.[10] The presence of benzonitrile in complex **2** is evidenced by two strong absorptions arising from C—H out-of-plane deformations at 759 and 715 cm^{-1}. The triflate group in complex **5** is characterized by intense absorptions due to the CF_3 and $S(=O)_2$ stretches.

TABLE I Infrared data for dicationic nickel complexes in the region 4000–400cm^{-1}

1(cm^{-1})	*2(cm^{-1})*	*3(cm^{-1})*	*4(cm^{-1})*	*5(cm^{-1})*	*Assignment*
2295(m)	2228(m)	2292(m)	2299(m)	2290(m)	$\nu(C{\equiv}N)$
2320(m)	2280(m)	2320(m)	2324(m)	2317(m)	$(\delta CH_3 + \nu CC)^a$
1066(s)	1042(s)	-	-	-	$\nu(XY_4^-)$
942(w)	932(w)	-	-	-	$\nu(XY_4^-)$
759(w)	547(w)	-	-	-	$\nu(XY_4^-)$
-	-	-	1247(s)	-	$\nu(CF_3)$
-	-	-	1180(s)	-	$\nu_{as}(S(=O)_2)$
-	-	-	1030(s)	-	$\nu(S{=}O)_2)$
-	719(s)	-	-	-	δ(C—H) out-of-plane
-	715(s)	-	-	-	δ(C—H) out-of-plane

[a] band combination[9].

Electronic spectral data for the dicationic nickel complexes in the region 200–1100nm are shown in Table II. The electronic spectra of the dicationic nickel complexes are characteristic of octahedral symmetry around the metal center. Ni(II) d^8 complexes exhibit four transitions [attributed to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^1E_g$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)]. The frequency ratio ν_3/ν_1 has values of 1.61 and 1.63 and the molar extinction coefficients are low, between 1.5 and 25.9. Those properties are well known and largely used as diagnostic of octahedral symmetries in nickel complexes.[11]

The magnetic moments of the dicationic nickel complexes are in the 2.6 to 3.6 BM range (Table III), being characteristic for the octahedral environment of nickel and confirming the proposed structure for these compounds.

RBS of the cationic nickel complexes has been applied to their elemental characterization since this technique overcomes the problems of hygroscopic properties of these materials (the analysis is performed under high vacuum conditions, excluding water and other impurities). From the relative intensities of the F, Ni, Cl and Zn signals we could calculate the F/Ni atomic ratio to the complexes $[Ni(MeCN)_6][BF_4]_2$ and $[Ni(PhCN)_6][BF_4]_2$ (8.6 ± 0.8 and 8.1 ± 0.8, respectively) and the Cl/(Ni+Zn) atomic ratio to the complex $[Ni(MeCN)_6]$ $[ZnCl_4]$ (2.0 ± 0.2).

It is obvious from the data (IR, UV-vis, Rutherford Backscattering Spectroscopy (RBS), and magnetic moments measurements) that the complexes can unequivocally be described as possessing octahedral symmetry around nickel, with six nitrile ligands in the metal coordination sphere and a corresponding counter ion. The data presented in Tables II and III exclude the possibility of BF_4 or $ZnCl_4$ coordination to the nickel center.

CONCLUSIONS

The present results show that a variety of dicationic nickel complexes with different counter-anions (BF_4^-, $AlCl_4^-$, $ZnCl_4^{-2}$, $CF_3SO_3^-$) and nitriles (MeCN and PhCN) can be prepared from simple nickel precursors with high yields. Chemical oxidation of metallic nickel has been replaced by (i) electrochemical oxidation of a nickel electrode, by (ii) methathetical halogen abstraction of nickel chloride with Lewis acids and by (iii) the reaction of nickel acetate with strong Brönsted acids. The performance of the new complexes in different catalytic reactions is in progress.

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TABLE II Electronic spectral data for dicationic nickel complexes. Solutions 0.3mM of the complexes in the corresponding nitriles as solvents

	1		*2*		*3*		*4*		*5*	
Transition Band	ν_{max}[a]	ε[b]	ν_{max}	ε	ν_{max}	ε	ν_{max}	ε	ν_{max}	ε
$^3A_{2g}\rightarrow{}^3T_{2g}$	10 352	7.0	10 504	12.0	10 384	6.3	10 427	6.33	10 526	5.4
$^3A_{2g}\rightarrow{}^1E_g$	13 928	2.2	13 850	3.4	14 620	14.6	13 947	1.5	15 106	6.9
$^3A_{2g}\rightarrow{}^3T_{1g}(F)$	16 920	6.8	17 182	11.2	16 978	14.9	16 978	5.5	17 007	8.7
$^3A_{2g}\rightarrow{}^3T_{1g}(P)$	27 624	14.3	28 902	25.8	27 778	16.5	27.397	7.8	27 778	25.9
ν_3/ν_1	1.63		1.63		1.63		1.63		1.61	

[a] ν_{max} (cm^{-1}); [b] ε(lmol^{-1} cm^{-1}); ν_3/ν_1 : frequency ratio between $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{2g}$.

TABLE III Magnetic moments of dicationic nickel complexes

Complex	*1*	*2*	*3*	*4*	*5*
μ_{eff}	3.0	3.6	2.8	3.4	2.6

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