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Synthesis and Characterization of High Oxidation State Nickel a-Benzoinoxime Complexes Generated by Ligand-Metal Redox Reaction

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SYNTHESIS AND CHARACTERIZATION OF HIGH OXIDATION STATE NICKEL α-BENZOINOXIME COMPLEXES GENERATED BY LIGAND-METAL REDOX REACTION

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ABSTRACT

The complexes of nickel α -benzoinoxime were prepared and isolated in the solid state with or without potassium persulfate. The complexes are noted, respectively, as complex B and complex A. They were characterized by elemental analyses, conductometry, polarography, infrared spectroscopy, UV-Visible spectrometry, nuclear magnetic reasonance (¹H NMR) and electronic paramagnetic reasonance (EPR). These techniques have shown the existence of the higher oxidation states of nickel complexed by α -benzoinoxime. The oxidation of nickel was due to an electronic exchange between the metal and the ligand. From these investigations, the formulas of these complexes were found to be (A): Ni(C₁₄H₁₁NO)₂(OH)₂ . H₂O and (B): Ni(C₁₄H₁₂NO₂)₂(OH)₂ . 1.5 H₂O. Two

separate synthese led to the same oxidation state for nickel, <u>i.e.</u> +IV. In the absence of the oxidant, the ligand was involved in a redox reaction which leads to differences in the physico-chemical properties (color, melting point, IR and ¹H NMR spectra) of the products.

INTRODUCTION

Oximes are the ligands that are the most frequently used in extractive and analytical chemistry. Some of them stabilize the higher oxidation states of nickel dimethylglyoxime (DMG). DMG is currently used in the (>+II), such as colorimetric titration of nickel. The red color of the Ni-DMG complex observed in alkaline medium typically characterize the +IV state of nickel¹. This +IV oxidation state is obtained by oxidation of Ni(+II) by the usual oxidants (halides, oxygen, persulfate, nitric acid, etc.). We have shown in a recent paper² for the first time that α -benzoinoxime (C₁₄H₁₃NO₂), a well known analytical extracting agent for molybdenum^{3,4}, tungsten^{5,6} and vanadium⁵ in acidic medium, in alkaline medium was capable to complex several other cations like iron, cobalt, copper and nickel. In the present paper, we have undertaken a careful study of the nickel α-benzoinoxime complexes obtained under different experimental conditions (pH, ligand/metal and oxidant/metal ratios). The redox process which occurs during the complex synthesis was studied.

RESULTS AND DISCUSSION

Pulse Polarography and Coulometry

This study was carried out in a pentanol-ethanol mixture (50-50 % vol.) and 0.1 M KSCN as supporting electrolyte. When the organic phase of the extraction of nickel in the absence of oxidant is submitted to a polarographic study, no signal is observed immediately, but a weak one appears after 24 h. In contrast, the organic phase of extraction of nickel previously treated by $K_2S_2O_8$ gives instantly a single, well defined and reproducible polarographic peak at - 1.27 V/SCE. Its

intensity increases with the nickel concentration. The reduction process, by coulometric measurement, was found to be monoelectronic. The voltammogram of the nickel complex extracted in the presence of K2S2O8 and carried out in propylene carbonate-acetonitrile mixture (50-50 % vol.) and 0.1 M lithium perchlorate as supporting electrolyte exhibits a cathodic peak at -1.4 V/SCE. The absence of an anodic signal reveals an irreversible system. The peak located at -2.0 V/SCE is attributable to the ligand reduction. The oxidation state of nickel in the extracted complex in the presence of oxidant was determined by a controlled potential electrolysis which was carried out in water-ethanol (50-50 % vol.) and 0.1 M LiClO₄ medium at -1.5 V/SCE. In this medium, the polarogram of the complex exhibits two successive peaks located at -1.22 and -1.57 V/SCE. The reduction processes are, respectively, mono and dielectronic. We attribuate these reductions, respectively, to Ni(III/II) and Ni(II/0) couples. The controlled potential electrolysis with a mercury pool electrode was run at -1.5 V/ SCE. This potential is reducing enough to reduce the oxidized nickel to Ni(II) α -benzoinoxime complex. The average value for n for the controlled potential reduction at the mercury cathode was 1.7. The reduction of Ni(IV) to Ni(III) is not observable in the studied electroreduction field (-0.4 to -1.7 V/SCE) and probably occurs at more positive potentials. The experimental value fell slightly short of the expected value, namely 2. This may be due to a decomposition of Ni(IV) to Ni(III) or to a mixture of the two states +IV and +III with a weak contribution of the latter. In fact, the bibliography mentions several oxidation states of nickel. The +III and +IV state are well stabilized by oximes under various conditions 7-13.

Magnetic Study

The complex B which corresponds to the +IV oxidation state is theoretically diamagnetic. However, it shows a moment of 0.867 M.B (Table I) attributable to a decomposition observed for analogue compounds¹¹. This decomposition is accompanied by the appearance of a paramagnetic species detected by the EPR study, namely a Ni(III) complex. The magnetic moment of the complex A varies until it reaches 0.835 M.B. We attribuate this increase to the progressive oxidation

Table I. Colors, Melting Points, Yields, Molar Conductivities and Magnetic Moments of the Complexes

| Complex | Color | Yield (%) | M.p °C | $\chi_{\rm M}(\Omega^{-1} {\rm cm}^2 {\rm mole}^{-1})$ | μ (Μ.Β) |
|---------|---------------|-----------|--------|--------------------------------------------------------|---------|
| A | yellow | 90 | 135 | 20.83 | 0.435 |
| B | yellow orange | 85 | 158 | 20.37 | 0.870 |

of Ni (II) to Ni (IV), probably with an intermediate paramagnetic state. Some physical properties of the complexes are reported in Table I.

Conductometric Study

The weak values of the molar conductivities carried out in DMSO (Table I) show a non-electrolytic nature of the complexes¹⁴.

EPR Study

The EPR study was perfomed in CHCl₃ for complex A and in the solid state for complex B. The spectrum of complex A presents a signal corresponding to a one-electron system with axial symmetry without superhyperfine structure. The spectrum of complex B is similar to that of complex A. The calculated parameters are:

complex A, $g_{1/} = 2.328$; $g_{\perp} = 2.002$; g = 2.111complex B, $g_{1/} = 2.280$; $g_{\perp} = 1.980$; g = 2.080where $g = 1/3g_{1/}+2/3g_{\perp}$

The g value (>2) shows that the signal is due to a complex of Ni(III) in a tetragonal environment. Opposite to the literature¹⁵, the lone electron is not localized to the dz² orbital. The $g_{//} > g_{\perp}$ situation is very rare in low-spin pseudo octahedral nickel(III) complexes. It corresponds to a $x^2 - y^2$ ground state. An axially compressed NiN₂O₄ or NiN₄O₂¹⁶ coordination sphere is frequently responsible of this unusual ground state. This study indicates clearly that the



Fig. 1. UV-Visible and near-infrared Spectrum (in CHCl₃) of the Nickel Extracted and Synthesized Without $K_2S_2O_8$. Nickel Concentration: (a): 10^{-2} M; (b): $2 \ 10^{-3}$ M; (c): $2.3 \ 10^{-3}$ M and (d): $5.1 \ 10^{-3}$ M.

Ni(III) complex is the paramagnetic species which is observed during oxidation of the Ni(II) complex or the Ni(IV) complex decomposition.

UV-Visible Spectroscopic Study

The spectroscopic study was carried out in chloroform (CHCl₃). The electronic absorption spectra were registred with 1 and 5 cm suprasil cells, respectively, in the visible and near-infrared ranges. The spectrum of the chloroform solution of extraction of nickel without oxidant exhibits an absorption



Fig. 2. UV-Visible and near-infrared Spectrum (in CHCl₃) of the Nickel Extracted and Synthesized With $K_2S_2O_8$. Nickel Concentration: (a): 7.8 10⁻³ M; (b): 2.6 10⁻³ M and (c): 7.4 10⁻³ M.

band at 430 nm ($\varepsilon = 145 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 520 nm ($\varepsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 1a). This spectrum is changing with time, and after 5 days, the 430 nm band disappears, the shoulder becomes a well defined band at 520 nm ($\varepsilon = 240 \text{ M}^{-1} \text{ cm}^{-1}$) and a new shoulder appears at 600 nm ($\varepsilon = 100 \text{ M}^{-1}\text{ cm}^{-1}$) (Fig. 1b). The same band positions are obtained with the chloroform solution of extraction of nickel in the presence of oxidant: a band at 520 nm and a shoulder at 600 nm (Fig. 2a). The spectra of the dissolved complexes (A and B) in chloroform are similar to the spectrum of the solution of the extracted nickel in the presence of the oxidant. They represent a band at 520 nm ($\varepsilon = 240 \text{ M}^{-1} \text{ cm}^{-1}$), a shoulder at 600 nm ($\varepsilon = 8 \text{ M}^{-1}$



Fig. 3. Evolution of the UV-Visible Spectrum of Complex A in CHCl₃. Nickel Concentration: (a): $2.5 \ 10^{-3}$ M and (b): 10^{-3} M.

cm⁻¹) (Fig. 1d and 2c). This spectrophotometric study shows without ambiguity the nickel oxidation in complex A. This oxidation is accompanied by a structure change, from square-planar to octahedral. The spectrum of freshly synthesized complex A dissolved in chloroform reveals a band at 440 nm and a shoulder around 520 nm (Fig. 3a). After a drying under argon during 15 days, complex A exhibits a new spectrum (a band at 520 nm and a shoulder at 600 nm) (Fig. 3b).

This study confirms the nickel oxidation by the ligand: an electronic exchange occurs between the metal and the ligand. This hypothesis is confirmed by the IR and ¹H NMR studies.

| | H ₂ O(free) | bound OH | C=N | N-O | C-0 | Ni-O | Ni-N |
|-----------|------------------------|----------|------|------|------|------|------|
| Ligand | | | 1491 | 1242 | 986 | | |
| Complex A | 3600 | 3200 | 1493 | | 1015 | 580 | 475 |
| Complex B | 3600 | 3200 | 1500 | 1228 | 1010 | 590 | 480 |

Table II. Characteristic IR Bands of the Ligand and the Complexes as KBr

Infrared Study

Pellets (cm^{-1})

The characteristic vibrations of the ligand and the complexes are summarized in Table II.

The shift of the C=N and C-O vibrations and the appearance of two new metal-ligands bands in the IR spectra of the complexes prove that the coordination occurs by both nitrogen and oxygen atoms. This implies the deprotonation of the hydroxylic group of the ligand (complex B). The disappearance of the N-O band for the complex A establishes the oxime reduction to an imine and, consequently, the nickel is oxidized. The coordinated H_2O molecules in the complexes are identified by the broad absorptions around 3600 cm⁻¹ due to the OH grouping.

¹H NMR Study

The chemical shift values of the ligand and the complexes are given in Table III.

The ¹H NMR spectrum of α -benzoinoxime exhibits two signals (10 protons) located between 7.13 and 7.33 ppm corresponding to the aromatic protons. It shows two doublets, the first one at 5.59 ppm and the second one at 3.72 ppm corresponding, respectively, to H-C-OH* and H*-C-OH. The value of the coupling constant of the two peaks (J = 5.23-5.3 Hz) indicates the existence of an interaction between the two protons. The OH of the oxime grouping is absent from the spectrum and this is probably due to a rapid exchange between the oxime and the solvent (CDCl₃). The spectum of complex B is similar to that of the oxime. It

| | δ (ppm) | Assignment | Coupling constant (Hz) |
|------------------------|---------------|------------|------------------------|
| | 7.13-7.16 (m) | H(arom) | |
| α -Benzoinoxime | 7.28-7.33 (m) | H(arom) | |
| | 5.59 (d) | н-с-он* | 5.2 |
| | 3.72 (d) | H*-C-OH | 5.3 |
| | | | |
| | 6.78-8.58 (m) | H(arom) | |
| Complex A | 3.65 (d) | H*-Ċ-O- | 20.0 |
| | 2.91 (d) | H*-C-NH2 | 18.0 |
| | 2.17(s) | bound OH | |
| | 1.26 (s) | -NH2 | |
| | | | |
| Complex B | 6.54-8.76 (m) | H(arom) | |
| | 3.75 (s) | H*-Ç-O | |
| | 1.86(s) | bound OH | |

Table III. ¹H NMR Data for the Ligand and the Complexes in CDCl₃ (ppm)

s: singlet d: doublet m: multiplet.

exhibits a broad peak corresponding to aromatic protons and two singlets located at 3.75 and 1.86 ppm attributable respectively to H*-C-O (1 proton) and the bound OH (1 proton). Complex A presents an ¹H NMR spectrum different from that of the oxime. It exhibits principally a peak at 1.26 ppm attributable to an amine grouping. It is well established¹⁷⁻¹⁸ that oximes generally are reduced to amines in which the N-O bond is cleaved before hydrogenation of the C=N double bond occurs. In acidic medium, the reaction is:

$$RR'C=NOH \xrightarrow{H^{+}} [RR'C=NOH]H^{+} \xrightarrow{+2 e^{-} + 2 H^{+}} RR'C=NH_{2}^{+}$$
$$\xrightarrow{+2 e^{-} + 2 H^{+}} RR'CHNH_{3}^{+}$$

We think that in solution (used for the ¹H NMR study), the same reaction may occur. The proportion of Ni(III) complex (detected by EPR) should be oxidized to Ni(IV) and, consequently, a certain number of C=N double bonds are reduced to amine (-NH₂) which is responsible of the signal observed at 1.26 ppm. The following reaction is proposed:

$$C=N-$$
 + 3 e⁻ + 3 H⁺ \longrightarrow $CH-NH_2$

The NMR spectrum, thus, corresponds to the superimposition of the NMR spectra of the two type of ligands (imine and amine). In this case, the solution contains only a diagmagnetic species and then a comparison between the NMR spectrum of complex A and the simulated one of the amine should be undertaken. The simulated spectrum of the amine mentioned above is similar to that of the complex A since it presents two signals between 7.1 and 7.4 ppm, two doublets at 5.55 and 4.35 ppm and lastly two singlets located at 2.8 and 1.6 ppm. This oxidation occurs by an electronic transfer between the metal and the ligand.

EXPERIMENTAL

Reagents

All reagents and solvents used in this study, nickel nitrate, potassium persulfate, α -benzoinoxime, ammonia, chloroform, pentanol, ethanol, propylene carbonate, acetonitrile and potassium thiocyanate are Fluka products for analysis.

Apparatus

The elemental microanalyses were carried out at the Central Service of Analysis, CNRS (Solaize-Lyon, France). Melting points were measured using a digital melting point apparatus. The conductimetric measurements were carried at room temperature with a CD 810 Tacussel conductivitymeter. UV-Visible and nearinfrared spectra were recorded on a Lambda 9 Perkin Elmer spectrophotometer using suprasil cells. Magnetic susceptibilities were obtained at room temperature with a B-SU 10 Bruker magnetic balance using $Hg[Co(SCN)_4]$ as paramagnetic reference. Diamagnetic correcctions were made using Pascal's constants. The ¹H NMR solution spectra in CDCl₃ were recorded at room temperature on a Bruker AM 300 spectrometer with TMS as reference. The EPR spectra were recorded with a Bruker ER 200 spectrometer. IR spectra were registred as KBr pellets with a Fourier Transform Infrared spectrophotometer F.T.S.7. Differential pulse polarographic curves and controlled potential electrolysis were recorded by using a Tacussel polarograph PRG₅ in a three-electrode system with a dropping mercury electrode, or a mercury pool as a working electrode, a satured calomel electrode as the reference (S.C.E.) and a Pt wire as a counter electrode. The voltammetric study was recorded on a Tacussel P.J.T 24-1 voltammograph with a hanging mercury electrode as a working electrode. All measurements were carried out at 20° C. Solutions were deaireted by a rapid stream of nitrogen.

Complexes Synthesis

In Solution. The Ni(II) α -benzoinoxime complex is extracted in one stage in a stoppered glass tube by shaking equal volumes (10 mL) of aqueous metal salt phase at 10⁻³ M (adjusted at pH = 10) with 10 mL of the organic phase (pentanol saturated with water) containing the oxime at 2x10⁻² M. For the synthesis of the complex in the higher oxidation state of nickel, we used Rama-Krushna Panda's work¹⁹. The process consists in mixing 1.5 mL of a solution of K₂S₂O₈ (2x10⁻² M) and 8.5 mL of the aqueous metal salt phase at 10⁻³ M. The pH is adjusted to 11 with ammonia. A black product precipitates. It was mentioned to be NiO₂. 3 H₂O²⁰. The oxidant/metal ratio is fixed at 3.5 for reaching complete oxidation. This suspension is extracted by 10 mL of the organic phase (pentanol saturated with water) containing the oxime at 2x10⁻² M. In both cases, the extraction phases are yellow.

<u>In The Solid State.</u> The complexes are isolated by precipitation from an ethanol-water mixture (50-50 % vol.)

In the absence of oxidant: the process consists of mixing 0.291 g (1mmole) of nickel nitrate, $Ni(NO_3)_2$. 6 H₂O, dissolved in 20 mL of distilled water and 0.682 g

| Complex | Formula | F. wt. | Calculated (Found) % | | | |
|---------|--------------------------------------------------------------------|--------|----------------------|--------|--------|---------|
| | | | C | H | Ν | Ni |
| A | C ₂₈ H ₂₆ N ₂ O ₅ Ni | 528,71 | 63.55 | 4.91 | 5.29 | 11.10 |
| | | | (63.25) | (4.75) | (5.25) | (10.80) |
| В | C ₂₈ H ₂₉ N ₂ O _{7,5} Ni | 571,71 | 58.77 | 5.07 | 4.89 | 10.26 |
| | | | (58.91) | (4.73) | (5.19) | (10.24) |

Table IV. Elemental Analysis Data of the Complexes

(3 mmoles) of α -benzoinoxime dissolved in 20 mL of absolute ethanol. The pH is fixed to 10 by ammonia. A yellow precipitate appears (complex A).

In the presence of oxidant: the process decribed above is used again but in the presence of potassium persulfate. It consists of mixing 0.81 g (3 mmoles) of $K_2S_2O_8$ dissolved in 20 mL of water with 0.291 g (1mmole) of nickel nitrate in the presence of ammonia (pH = 11). A black product (NiO₂ · 3 H₂O) precipitates. It disappears when 20 mL of the ethanolic α -benzoinoxime solution (3 mmoles) is added and then a yellow orange precipitate appears (complex B). The complexes are filtered, washed with water and ethanol-water mixture and dried at 80° C. According to the elemental analysis results (Table IV), the following formulas: Ni(C₁₄H₁₁NO)₂(OH)₂ , H₂O and Ni(C₁₄H₁₂NO₂)₂(OH)₂ . 1.5 H₂O are found, respectively, for the complexes A and B. Unfortunately, we could not obtain any single crystal for the complexes suitable for X Ray cristallographic study.

From all the investigations, we propose the processes in Fig. 4 for the formation of the complexes.

Conclusion

In this study, we have shown that nickel complexed by α -benzoinoxime is oxidized by the ligand without using other oxidants. The existence of the higher oxidation states of nickel and the modification of the ligand structure has been





Fig. 4. Formation and Suggested Structures of the Complexes.

noted on the basis of UV-Visible, infrared, EPR,¹H NMR and magnetic data. The difference in the physico-chemical properties between the two complexes (in the solid state) has not been revealed by the UV-Visible study but by the use of other techniques, such as the infrared and NMR.

We have also shown that α -benzoinoxime (an hydroxyoxime) has played the same role as dioximes, stabilizing the higher oxidation state of nickel.

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