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Coordination Compounds of Ni^{II} and Ni^{III} with Paludrine

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The coordination compounds of Ni^{II} and Ni^{III} with paludrine(N^1-p-chlorophenyl-N^5-isopropylbiguanide)are presented. There have been obtained nickel mono-, di-, and trichelates of the type: $[Ni\,pald\,X_n]$, $[Ni\,pald_2(OH_2)_2]X_n$ and $[Ni\,pald_3]X_n$ where $n=2,3$. Mention is made that for the first time Ni^{III} compounds with paludrine have been synthesized by $NaClO_2$ oxidation in nonaqueous solvents. The magnetical determinations, the visible and UV absorption spectra, the reflexion spectra, the polarographic as well as the reductions with various chemical agents, allowed the characterization of these compounds and confirmed the high valence state of nickel.

Introduction

The speciality literature[1,2,3] comprises data on the tendency of Ni^{II} to form coordination compounds with some substituted biguanides of the form $[NiL_2]X_2$.

As concerns the high valence stages of this element, mention is made in the literature[4-10] of Ni^{III} or Ni^{IV} coordination compounds with various ligands: phosphine, arsine, glyoxime, carborane, a.s.o.

Lately we have made known the first data[11,12] on the formation of Ni^{III} coordination compounds with biguanide derivatives of the type: $[Ni(RBig)_3]X_3$ and $[Ni(RBig)_2(OH_2)_2]X_3$ by using the oxidation with $NaClO_2$ of the corresponding Ni^{II} compounds in ethanol, dimethylformamide or dimethylsulfoxide.

The present paper aims at presenting both the obtention of new Ni^{II} and Ni^{III} coordination compounds with paludrine and the study of the chemical, magnetical, and spectrochemical properties in view of establishing their structure.

Experimental Section

Materials. Paludrine-(pald)(N^1-*p*-chlorophenyl-N^5-isopropylbiguanide), $NiCl_2 . 6H_2O$ and $Ni(NO_3)_2 . 6H_2O$ Merck p.a. have been used as ligand.

The anhydrous nickel(II) chloride has been obtained by dehydration of $NiCl_2 . 6H_2O$ with thionyl chloride.[13]

Methanol, absolute ethanol, dimethylformamide (DMF) dried on molecular sieves and freshly distilled dimethylsulfoxide (DMSO) have been used as solvents.

Preparation of Nickel(II) Coordination Compounds. A mixture of anhydrous $NiCl_2$ (lg) and N^1-*p*-chlorophenyl-N^5-isopropylbiguanide, molar ratio 1:1, is refluxed for 2 hr in 10 ml DMF. After cooling it is filtered and on treatment with absolute ether in excess a crystalline compound separates.

The raw product is purefied by treating it with absolute alcohol until the filtrate turns green to yellow. $[Ni\,pald\,Cl_2]$ as pale-yellow crystals separates.

By heating a $NiCl_2 . 6H_2O$ solution with N^1-*p*-chlorophenyl-N^5-isopropylbiguanide, molar ratio 1:2, in ethanol, $[Ni\,pald_2(OH_2)_2]X_2$ is formed; when the solution's pH ranges from 6.5 to 7 after solvent's evaporation, the series' chloride separates, while at pH=8-9, using KOH in ethanol, the series' base separates.

Concentrated $NiX_2 . 6H_2O$ and N^1-*p*-chlorophenyl-N^5-isopropylbiguanide solutions in absolute ethanol (where $X=Cl^-$, NO_3^-), molar ratio 1:3, after mixing and heating become deep red. Red-orange $[Ni\,pald_3]$-X_2 crystals appear after ice-cooling.

Preparation of Ni^{III} Coordination Compounds. Concentrated $[Ni\,pald\,Cl_2]$, $[Ni\,pald_2(OH_2)_2]X_2$ (where $X=OH^-$, Cl^-) or $[Ni\,pald_3]Cl_2$ solutions in DMF have been treated with solid $NaClO_2$. The solution turns brown after slight heating up to approximately 40°C, and the pH remains at 7-8 with KOH in ethanol. After cooling, it is treated with a great ether excess (50:1) when, after vigorous stirring, brown crystals separate on ice. These are filtered off washed with a small amount of cold water and vacuum dried on P_2O_5.

Determinations of Magnetical Susceptibility. Magnetical measurements have been achieved according to Gouy's method using a standard substance, Hg^{II}

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Table I. Analitical Data

Compounds	Colour	Ni %		N_t %		Cl %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
[Ni pald Cl_2] .	yellow-pale	15.32	15.18	18.27	18.10	18.50	18.80
[Ni $pald_2(OH_2)_2$]Cl_2	yellow-orange	8.72	8.76	20.81	20.60	10.53	10.80
[Ni $pald_3$]Cl_2	red-orange	6.59	6.70	23.58	23.49	7.96	8.03
[Ni $pald_3$]$(NO_3)_2$	red-orange	6.22	6.19	25.22	25.02	—	—
Ni pald Cl_3	brown	13.92	13.70	16.61	16.54	25.22	25.40
[Ni $pald_2(OH_2)_2$]$(OH)_3$	brown	8.98	9.08	21.45	21.24	—	—
[Ni $pald_3$]Cl_3	brown	6.34	6.18	22.68	22.42	11.48	11.60

tetrathiocyanocobaltiate(II). The magnetical moments have been calculated in accordance with the following expression: $\mu_{eff}=2.84\sqrt{\chi_M \cdot T}$.

Spectrophotometric Measurements. The visible absorption spectra, the UV spectra in solution as well as reflexion spectra have been run on a universal VSU_1 spectrophotometer in the 220-800 nm range, by using solutions in methanol, DMF and DMSO.

The Polarographic Reductions have been preformed on an LP-60 polarograph, with DMF solutions.

Results and Discussion

Nickel Coordination Compounds (d^8). This paper summarizes the results on the nickel (d^8) tendency to form with paludrine, disubstituted biguanide which usually acts as bidentate ligand, mono-, di-, and tri-chelates of the type: [Ni pald Cl_2], [Ni pald$(OH_2)_2$]-X_2, and [Ni $pald_3$]X_2.

By the paludrine action on anhydrous $NiCl_2$ we separated the first monobiguanide coordination compound as crystalline, pale-yellow powder, soluble in DMF, DMSO and sparingly soluble in ethanol. The analytical data (Table I) show that the compound is a monochelate [Ni pald Cl_2], with planar structure confirmed by its diamagnetical character.

As dichelate coordination compound, we suceeded in obtaining $[NiL_2(OH_2)_2]X_2$ compounds.

The experimental data show that Ni^{II} preferentially forms octahedral dichelates of the form [Ni $pald_2(OH_2)_2$]X_2, with paludrine.

The [Ni $pald_2(OH_2)_2$]$^{2+}$ cation may be obtained either by the paludrine's action on $NiX_2 \cdot nH_2O$ at pH=7-7.5 or on $[Ni(NH_3)_6](OH)_2$.

All dibiguanide coordination compounds are crystalline, yellow-orange powders, stable in air both in the solid state and solution, soluble in DMF, DMSO and partly soluble in alcohol.

The magnetic moment determinations run with these compounds (Table II) (where $\mu_{eff}=2.6$-2.9 BM) confirm that the octahedral structure for these Ni^{II} dichelates agrees with the data in the literature[14,15] which assume magnetical moments ranging from 2.4-3.2 BM for Ni^{II} dichelates with other ligands.

Given the octahedral structure we consider the two paludrine molecules as being in the same plane, and the two water molecules in a *trans* position. This statement is supported also by the fact that oxidation facilitated the separation of [Ni $pald_2(OH_2)_2$]X_3 compouds.

Table II. Room temperature magnetic moments (BM)

Compounds	Temperature (°K)	μ_{eff}
[Ni pald Cl_2]	297	0.07
[Ni $pald_2(OH_2)_2$]Cl_2	293	2.64
[Ni $pald_3$]Cl_2	297	2.71
Ni pald Cl_3	297	1.63
[Ni $pald_2(OH_2)_2$]$(OH)_3$	297	1.69
[Ni $pald_3$]Cl_3	297	1.78

The presence of the [Ni $pald_3$]$^{2+}$ cation is characterized by a deep red colour of the alcoholic, concentrated NiX_2nHO_2-paludrine solutions.

The [Ni $pald_3$]X_2 trichelates show an octahedral structure confirmed by magnetical moments around 2.7 BM and may be $NaClO_2$ leading to Ni^{III} trichelate coordination compounds.

The possible resolution of optical antipodes of these compounds is being investigated at present.

The absorption spectra carried out on all Ni^{II} compounds in methanol and DMF solutions as well as the reflexion spectra present two bands, the former a visible one, ~450 nm (~22,000 cm^{-1}) (Figure 1,

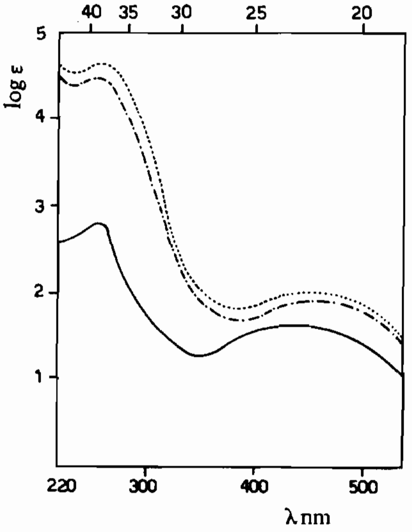

Figure 1. Visible and ultraviolet spectra of coordination compounds of Ni^{II}, in methanol. ——, [Ni pald Cl_2]; — · —, [Ni $pald_2(OH_2)_2$]Cl_2; . . . , [Ni $pald_3$]Cl_2.

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Figure 2, Table III) and the latter at 260 nm (~39,000 cm^{-1}).

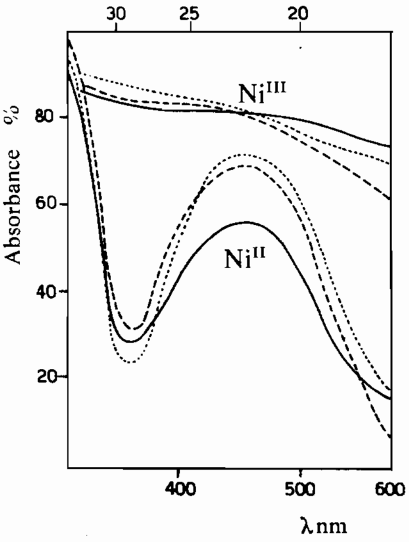

Figure 2. Solid state spectra in reflectance of compounds. ——, [Ni pald Cl$_n$]; – – –, [Ni pald$_2$(OH$_2$)$_2$](OH)$_n$; . . . , [Ni pald$_3$]Cl$_n$, where n=2, 3.

Table III. Spectral data of ligand and its coordination compounds of Ni^{II}

Compounds	λ$_{max}$ (nm)	λ$_{max}$ (cm^{-1})	log ε$_{max}$	Absorbance %
Paludrine . HCl	259	38,610	4.45	—
	232	43,100	4.27	—
[Ni pald Cl$_2$]	448	22,320	1.60	—
	258	38,760	4.53	—
	460	21,740	—	56.50
	260	38,460	—	95.90
[Ni pald$_2$(OH$_2$)$_2$]Cl$_2$	456	21,930	1.83	—
	256	39,060	4.48	—
	464	21,550	—	70.00
	260	38,460	—	95.90
[Ni pald$_3$]Cl$_2$	454	22,030	2.08	—
	258	38,760	4.71	—
	460	21,740	—	74.20
	258	38,760	—	95.30

All mono-, di-, and trichelate coordination compounds have the same band in the visible range (transition *d–d*) corresponding to the d^8 configuration; the second ligand band in the remote UV is shifted below 220 nm.

Ni(d^7) Coordination Compounds. According to the experimental part, the present paper deals with a general method allowing to obtain Ni^{III} coordination compounds with paludrine, *i.e.* the NaClO$_2$ oxidation of corresponding Ni^{II} compounds in DMF at pH=7-8 leading to mono-, di-, and trichelate compounds of the type: Ni pald Cl$_3$, [Ni pald$_2$(OH$_2$)$_2$]X$_3$ and [Ni pald$_3$]X$_3$. It should be however mentioned that the oxidant does not influence the ligand (paludrine) as resulted also from the study on the coordination compounds of other elements in the 3*d*, 4*d*, 5*d* series at higher valence stages.

The analytical data (Table I) make possible the above formulation. The [Ni pald$_2$(OH$_2$)$_2$]$^{3+}$ and [Ni pald$_3$]$^{3+}$ cations are stable in nonaqueous solvents and may be removed as sparingly soluble compounds by using the anions: Br$^-$, I$^-$, CNS$^-$, CNO$^-$, N$_3^-$, ClO$_2^-$, ClO$_4^-$, [Cr(SCN)$_6$]$^{3-}$, [Cr(NH$_3$)$_2$(SCN)$_4$]$^-$.

All Ni^{III} coordination compounds with paludrine are hardly soluble in water, benzene, carbon tetrachloride and soluble in methanol, ethanol, dioxane, glycerine DMF, DMSO a.s.o.

The stability of these compounds is quite remarkable both in the solid state and in methanol DMF, DMSO solution.

It should be noticed that in the presence of various reducing agents such as NaH$_2$PO$_2$, SnCl$_2$, KBH$_4$, N$_2$H$_4$.HCl in alcohol, these compounds indicate the reduction of Ni^{III} to Ni^{II} by conversion of the solution from brown into yellow. In some cases even Ni^{II} compounds with paludrine, which we identified by direct methods, could separate. The use of [BH$_4$]$^-$ in aqueous medium leads to metallic nickel.

By following polarographically the Ni^{III} reduction to Ni^{II}, the polarograms show only one reduction stage according to the system reversible in DMF:

$$[\text{Ni pald}_3]^{3+} \rightleftharpoons [\text{Ni pald}_3]^{2+} + 1e$$

The reflexion spectra (Figure 2) carried out on powders in the 220-800 nm range as well as the absorption spectra in either methanol or DMF solutions, prove that no interaction occurs between solvent and compounds, the curves being similar for both cases and a visible continous absorption characteristic also of other coordination compounds taking place at higher valence stages. For the UV range the ligand's band is around 260 nm.

Our formulation is supported also by the magnetical determinations (Table III) achieved on samples of various syntheses, at room temperature, with values in the range 1.66-1.78 BM.

For Ni^{III} coordination compounds with various ligands, the literature[4,5,6,7,10] shows values ranging from 1.65 to 1.94 BM.

It is well known that the magnetic criterion is not sufficient for the elucidation of the structure, its combination with other physical and chemical methods being highly necessary.

According to our data on the Ni^{III} coordination compounds with paludrine, we regard the [Ni pald$_2$(OH$_2$)$_2$]X$_3$ and [Ni pald$_3$]X$_3$ coordination compounds as possessing an octahedral configuration (d^{2}sp^3), while the Ni pald X$_3$ compounds is liable to either a tetragonal pyramid structure or to a trigonal bipyramid. The EPR and X-ray data allow to elucidate these structures.

A forthcoming paper will comprise data on the application of the NaClO$_2$ oxidation method also to nickel compounds with higher valence stages, with *o*-phen, dipy, other dibiguanide and triguanide derivatives.