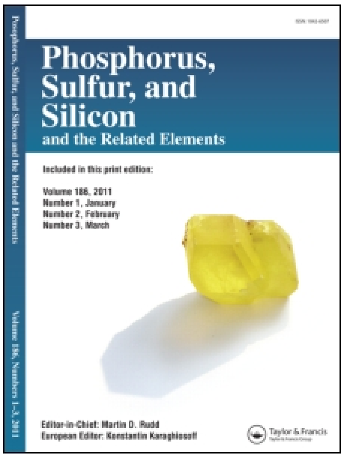

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Synthesis and Study of New Clathrochelates with 1-Phenyl-2-(1'-Piperidinyl) Ethanone Oxime Ligand

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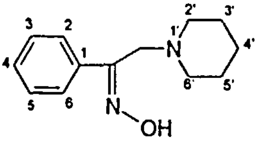
The synthesis and characterization of new complex compounds of $[M(L\text{-}H)X_2]$, $[ML(L\text{-}H)]X$ and $[M(L\text{-}H)_2]$ types (M= Co, Ni, Cu, X = Cl, CH_3COO) and L=1-phenyl-2-(1'-piperidinyl) ethanone oxime is presented. In reactions of $[ML(L\text{-}H)]X$ (M = Ni, Cu) with Lewis acids like $TiCl_4$ and $SnCl_4$ semiclathrochelates of $[M(L\text{-}H)_2M'Cl_2]$ type (M' = Ti, Sn) were obtained and characterized (electronic, FT-IR, RPE, NMR spectra, conductivity measurements, as well as TD-analysis). Such complexes should be potential oxygen molecular carriers.

Keywords: Oximato metal complexes; semiclathrochelates

INTRODUCTION

The oxime or oximato metal complexes have been extensively studied not only from the point of their traditional synthetic routes, structural aspects and analytical applications, but also for their high reactivity. Thus, a variety of clathrochelates (biscapped tris-dioximates) or semiclathrochelates monocapped tris –dioximates) of Fe(II, III), Co(II, III), Ni(II), Ru(II) with B, Si, Ge, Sn and Sb as a "cap" have been isolated and characterized [1,2].



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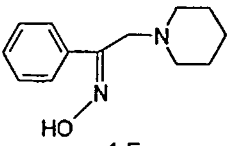

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The objectives of this paper were: synthesis and characterization of new complexes with **1**; reactions of some oximato complexes with Lewis acids like $TiCl_4$ and Sn Cl_4.

EXPERIMENTAL

A. LIGAND SYNTHESIS: The oxime **1** was prepared from the corresponding β-aminoketone [3] on treatment with $NH_2OH{\cdot}HCl$ in CH_3OH as solvent in the presence of NaOH. The mixture obtained contained more than 80% Z isomer, which has been purified. Spectral data are in agreement with literature [4]. The **1**-Z oxime has the following characteristics: *m.p.* 119-120°C; **IR Spectrum** (KBr, cm^{-1}):3263w, 3150m, 3079m, 3049m, 3026m, 2947s, 2929s, 2857s, 2811s, 2769s, 1453m, 1314m, 1192m, 999m, 977s, 762m, 695s; **^{1}H-NMR Spectrum** ($CDCl_3$, δ ppm): 1.48 (ls, 2H, $H_{4'}$), 1.65 (qv, 4H, $H_{3',5'}$, J = 14 Hz), 2.57 (ls, 4H, $H_{2',6'}$), 3.74 (s, 2H, CH_2), 7.35-7.37 (m, 3H, H_{3-5}), 7.60-7.62 (m, 2H, $H_{2,6}$), 11.5 (ls, 1H, NOH); **^{13}C-NMR Spectrum** ($CDCl_3$, δ ppm): 23.66 ($C_{4'}$), 25.68 ($C_{3',5'}$), 54.02 ($C_{2',6'}$), 58.09 (C_{CH2}), 126.05 ($C_{3,5}$), 128.50 ($C_{2,6}$), 129.21 (C_4), 136.01 (C_1), 153.37 ($C_{C=NOH}$).

B. SYNTHESIS OF COMPLEXES: All the complexes have been prepared in reflux at MX_2 : oxime molar ratios 1 : 1 or 1 : 2 in a mixture of water: methanol 1 : 1 as solvent. After ~2 hours of boiling solid products have been separated from solutions. The colored products were filtered, washed with methanol, and dried in a desiccator over P_4O_{10} (70-80% yields).

RESULTS AND DISCUSSION

In the described conditions, three different types of complexes have been prepared: [MLX_2], (M = Co, Ni, Cu; X = Cl, CH_3COO); [ML(L-H)]X, (M = Ni, Cu; X = Cl); [$M(L-H)_2$], (M = Ni, Cu), where L = **1**.

The bidentate nature of ligand **1** in all types of complexes was confirmed by the physico-chemical analyses of the complexes (elemental analysis, molar conductivity measurements, spectral data).

The electronic spectra of all cobalt complexes show two-bands (at 15.38-15.74 kK and 8.30-8.47 kK respectively), which are characteristic to $3d^7$ configuration in a tetrahedral symmetry field.

The two bands from the electronic spectra of nickel complex compounds (at 15.62-16.10 kK and 26.80-27.77 kK respectively) are specific for square planar geometry.

TABLE 1 Melting point and molar conductivity of the studied complexes

Complex	M. p. (°C)	Mol. cond. $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$	Type of electrolyte
$[CoLCl_2]$	185	2	non-electrolyte
$[NiLCl_2]$	170	10	non-electrolyte
$[CuLCl_2]$	195	12	non-electrolyte
$[CoL(CH_3COO)_2]$	180	3	non-electrolyte
$[NiL(CH_3COO)_2]$	210	20	non-electrolyte
$[CuL(CH_3COO)_2]$	195	20	non-electrolyte
[CoL(L-H)]Cl	215	85	1 : 1
[NiL(L-H)]Cl	200	90	1 : 1
[CuL(L-H)]Cl	230	90	1 : 1
$[Ni(L\text{-}H)_2]$	190	15	non-electrolyte
$[Cu(L\text{-}H)_2]$	195	15	non-electrolyte

10^{-3} M solution in DMF, 25°C

TABLE 2 Electronic spectra and spectral parameters

Complex	Color	Bands (kK)	Assignement	10Dq	B(kK)	β
$[CoLCl_2]$	green	15.38; 8.30	$^4A_2\rightarrow{}^4T_1(F)$, $^4A_2\rightarrow{}^4T_1(P)$	4.93	0.650	0.669
$[CoL(CH_3COO)_2]$	dark-green	15.50; 8.47	$^4A_2\rightarrow{}^4T_1(F)$, $^4A_2\rightarrow{}^4T_1(P)$	4.80	0.638	0.657
[CoL(L-H)]Cl	dark-green	15.74; 8.40	$^4A_2\rightarrow{}^4T_1(F)$, $^4A_2\rightarrow{}^4T_1(P)$	4.75	0.659	0.679
$[NiLCl_2]$	yellow	15.62; 27.77	$b_{1g}\rightarrow b_{2g}$, $b_{1g}\rightarrow a_{1g}$	-	-	-
$[NiL(CH_3COO)_2]$	light-orange	15.90; 26.80	$b_{1g}\rightarrow b_{2g}$, $b_{1g}\rightarrow a_{1g}$	-	-	-
[NiL(L-H)]Cl	light-orange	15.75; 27.20	$b_{1g}\rightarrow b_{2g}$, $b_{1g}\rightarrow a_{1g}$	-	-	-
$[Ni(L\text{-}H)_2]$	orange	16.10; 27.10	$b_{1g}\rightarrow b_{2g}$, $b_{1g}\rightarrow a_{1g}$	-	-	-

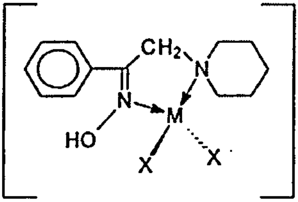
The ν_{OH} characteristic frequencies present in the IR spectra of oxime disappear in the spectra of $[M(L\text{-}H)_2]$ complexes but appear in the spectra of $[MLX_2]$ and [ML(L-H)]X complexes at about the same values. The $\nu_{C=N}$ exocyclic and $\nu_{C=N}$ cyclic frequencies from IR spectra of ligand are shifted and splitted in the spectra of all complexes as a proof of coordination of these groups to the metals (Table 3).

TABLE 3 The IR characteristic frequencies for Cu(II) complexes

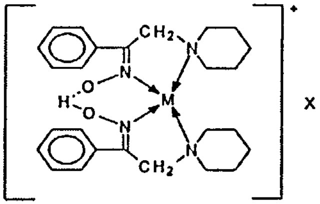
Complex	$\nu_{OH\,s}$, $\nu_{OH\,as}$	$\nu_{C=N}$	δ_{OH}	$\nu_{CN\,cycl}$	$\nu_{N\text{-}O}$
L	3450, 3120	1670	1450	1310	950, 980
$[CuLCl_2]$	3200	1660	1455	1330, 1370	920, 950
$[CuL(CH_3COO)_2]$	3150, 3100	1650; 1640	1460	1310, 1330	920, 930
[CuL(L-H)]Cl	3030	1640; 1650	1455	1330, 1280	950
$[Cu(L\text{-}H)_2]$		1640		1280, 1300	970, 980

By the reaction of [M(L-H)L]Cl complexes with $M'Cl_4$ (M' = Ti, Sn) semiclatrochelates $[M(L\text{-}H)_2M'Cl_2]$ were obtained. The structural formulae proposed for the three types of complexes and for clatrochelate are:

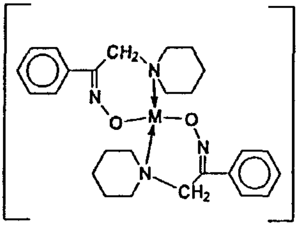
$[MLX_2]$



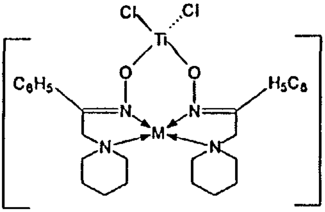
$[ML(L\text{-}H)]X$



$[M(L\text{-}H)_2]$



$[M(L\text{-}H)_2M'Cl_2]$



These formulae are also sustained by TG-DTG analysis (figure 1), the end products of the complexes decomposition being $CuCl_2$ (a), $NiCl_2$ (b) and $NiCl_2 + TiOCl_2$ (c)

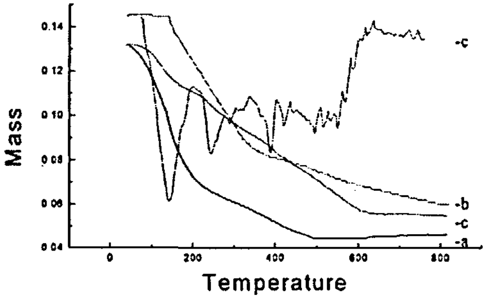


FIGURE 1 TG and ATG analysis of a) $[CuLCl_2]$; b) $[NiL(L\text{-}H)Cl]$; c) $[Ni(L\text{-}H)_2TiCl_2]$

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