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Synthesis And Characterisation Of Some Lanthanide Ion(III) Complexes With Mixed Ligands (Nicotinamide And Benzimidazole)

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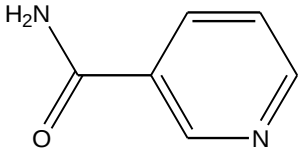
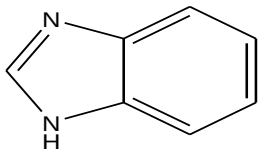
Complexes of Lanthanide ione Ln(III) =La(III) , Ce(III),Pr(III) and Nd(III) with ligands of nicotinamide (na) and Benzimidazole (BIMD) have been prepared with general formula [M(na)3(BIMD)3](NO3) where :
M = Ln(III) = La(III) , Ce(III) , Gd(III) , Nd(III) .
Na = nicotinamide = C7H6N2O
BIMD = Benzimidazole = C7H6N2
All compounds have been characterized by spectroscopic methods [FT-IR , UV-VIS , AAS] , microanalysis (C.H.N) Along with conductivity measurements , solubility , melting point , theroitical measurment by using chem office 3D prog .
Model (2000) .
Frome the above data the proposed moleculer structure for all complexes with its ions is octahydral geometries .

Introduction

Recently , there has been significat medicinal intrest in the coordination chemistry , the structure properties and the reactivity of metal complexes of nicotinamide (na) [1-4] snd benzimidazole (BIMD) derivatives are usefuf as fungicides , anthilimintcs and becteriocides [5-6] . Mostly owing to its function as electron acceptor in some enzymatic reactions . [7]
There is growing pharmaceutical and chemical interest in compounds contaning the benzimidazole and nicotinamide . [8-13] .

Aseries of mixed ligand contaning nicotinamide and saccharinato complexes (14-17) .
Tabel (1) show some properties of tow ligands (nicotinamide and benzimidazole) .

Chemical name	**Nicotinamide**	**Benzimidazole**
Symbol	na	BIMD
Chemical structure		
Molecular formula	$C_6H_7N_2O$	$C_7H_6N_2$
Molecular weight	122.12	118.14
m.p	130.00-133.00 deg ^{0}C	172 ^{0}C
Physical state	Crystalline powder	Crystalline powder
appearance	white	White - yellow

We report here the preperation and structural analysis of the Ln(III) complexes of mixed ligands (nicotinamide and benzimidazole) .

Experimental

A. Reagents and instruments : Nicotinamide , Ce(NO3)3.6H2O , Pr(NO3)3.6H2O , La(NO3)3.6H2O , were purchased from (Merck) , benzimidazole and solvents from (B.D.H) . the reagents were applied without further purification .

The FT-IR spectra were recorder using pressed KBr pellets with fouirer transform infrared spectro photometer shimadzu 24 FT-IR-8300 . Electronic spectra were recorded on shimadzu-Uv-160A ultra violet visible spectrophotometer in the (200-1100) nm rage at 1cm cell length for 10^{-3} solution in DMF at 25 ^{0}c .

Complexes were determined by atomic absorption (AAS) technigue using Japan AA-670 shimadzu .

Melting points were recorded by using stuart melting point apparatus .

Electrical conductivity measuments of the complexes were recorded at 25 0c for 10-3 m solutions of the sample in DMF using pw 9527 digital conductivity meter (Phlips) .

The modelling package chem 3D prog (ver 3.5.2) model (2000) .

B. General Synthesis :

The compounds were prepare by addition of nicotinamide and benzimicazole to warm stirred aqueous solution of the respective metal (III) nitrate in the stoichimetric ratio . after cooling of the solution , pale violet well-shaped crystasls of the Nd(III) compounds , pale yellow crystal of the Ce(III) compounds , pale-green crystals of the Pr(III) and colourless crystals of the La(III) . Were obtain . The crystals were filtered , washed with acetone and dried at room temperature . (12) .

Resulta And Discussion :

Physical properties and elemental analysis are listed in table (2) . All complexes dissolve in DMF solvent .

The electronic spectra :

The electronic spectra of all compound (Ligands and complexes) are listed in table (3) . The (uv-vis) spectrum of the free ligand (BIMD) in DMF solvent show a high intensity band wich is splited into two component with maximum absorption of wave number 36390.101 cm^{-1} and 35688.79 cm^{-1} attribution to (Π-Π*) transitions at 28506.271 cm^{-1} assigned to (n-Π*) transitions . [13] and free ligand (nicotinamide) (na) show a high intensity band in wave length 276 nm (3623 cm^{-1}) max (626 $l.mol^{-1}.cm^{-1}$) assigned to (Π-Π*) Fig1 [18] in addition to these transitions the spectra of the complexes axhibited another new bands in the visible region caused by chargetransfer (C.T) assigned to (F-F) transitions between the metal ion and the ligands . [19]

Fourier transform infrared spectra :

The assignment of some of the most characteristic FT-IR bands of four complexes is shown in table (4) .

The analysis of the spectra was performed in coparison with those ligand (benzimidazole , nicotinamide) and the previously investigated complexes (21 , 13 , 20) .

The spectra of the free ligands (nicotinamide , benzimidazole and $[Nd(BIMD)_3(na)_3]^{+3}$ are given in Figs.2 and 3 , respectively . Table (4) shows several vibrational modes of nicotinamide have shifted to higher frequency when compared with the free ligands .

Theoretical calculations :

Studying complexes on bases of the above analysis , the existence of hexacoordinated $[Ln(na)_3(BIMD)_3]^{+3}$, Ln(III) = La(III) , Ce(III) , Gd(III) and Nd(III) molecules .

A proposed models of these species were built with chem 3D (21) . The Ln(III) complexes ions resulted in centrosymmetric octahydral geometries Fig.3 while the fuor strucurally equivalent nicotinamide molecules with their pyridine nitrogen atoms approach from the apexes . In the model , the amide group is not caplaner with the pyridine ring [22,23] . The small differences in the unit cell volumes of the four complexes can be clearly correlated with the differences in the ionic of the cataions [ri La^{+3} (1.061)>ri Ce^{+3} (1.034)>ri Gd^{+3} (0.938)>ri Nd^{+3} (0.995)] . These differences are also reflected in the metal-to ligand bond distances as show in table (5) .

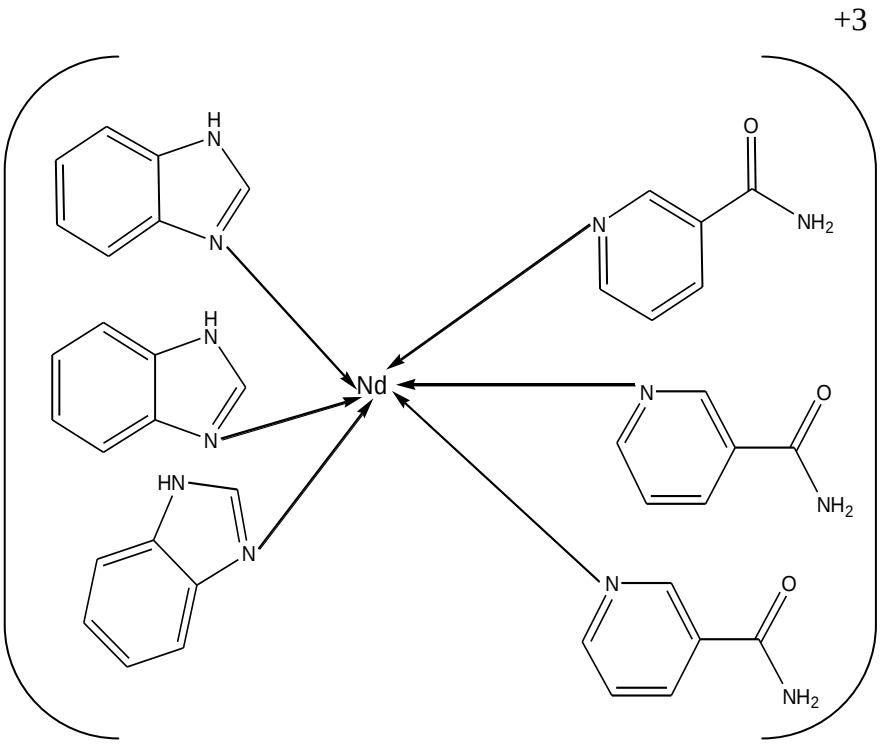


Fig.3 The suggested structure for the complexes $[Nd(na)_3(BIMD)_3]^{+3}$

Table (2) : Analysis and physical data of the complexes

complexes	mwt	colour	m.p°c	m.c* $s.cm^2 mol^{-1}$	Elemental analysis Found % (calculate %)			
					C %	H %	N %	Metal %
La[$C_{39}H_{36}N_{12}O_3$]	859.69	White	250d	7.83	54.49 (53.02)	4.22 (4.02)	19.55 (18.56)	16.16 (16.02)
Ce[$C_{39}H_{36}N_{12}O_3$]	860.90	White-yellow	>260	5.45	45.41 (53.86)	4.21 (3.82)	19.52 (18.66)	16.28 (15.99)
Gd[$C_{39}H_{36}N_{12}O_3$]	878.03	Pale-yellow	>260	8.36	53.53 (52.39)	4.13 (3.96)	19.14 (18.87)	17.91 (19.29)
Nd[$C_{39}H_{36}N_{12}O_3$]	865.02	Pale-violet	>260	8.50	54.14 (54.02)	4.22 (4.03)	19.55 (19.08)	16.67 (16.00)

Nomenclature of prepared complexes :

Table (6) shwo emirical formula and nomenclature (IUPAC) with Abbreviated .

Table (3) : Electronic Spectra of the studied complexes and two ligands

compounds	λ(nm)	Abs	ν(cm^{-1}) wave number	ε Max (l.mol-1.cm-1)	Assignment of the transition
Nicotinamide (na)	276	0.629	3623	629	π - π*
Benzimidazol (BIMD)	274.8 280.2 350.8	2.498 2.33 0.10	36390.10 35688.79 28506.27	2498 2339 100	π - π* π - π* n - π
$[La(BIMD)_3(na)_3]^{+3}$	294	1.124	34013.60	1124	C.T
$Ce(BIMD)_3(na)_3$	278	0.994	35971.22	994	C.T
$Gd(BIMD)_3(na)_3$	326 436 484	0.360 1.02 0.019	30674.84 22935.77 20661.15	360 102 19	C - T F - F F - F
$Nd(BIMD)_3(na)_3$	284 330 424	0.980 1.613 0.998	35211.26 3030.03 23584.90	980 1613 998	π - π* C.T F - F

Table (4) : Assignment of the most characteristic FT-IR bands of the studied complexes

compounds	NH_2 (asy) (str)	NH_2 (sym) (str)	CH (str) (Py)	C=O (str) (am)	NH_2 def (am)	Ring (str) (Py)	C-C (str) (Py)	CN (str) (am)	i.P (str) (Py)	NH2 Rock	O=CN bend (am)	ν CH arom	ν C=C	M-N	M-O
na	3360 vs	3299 s	3058 sh	1699 vs 1683 sh	1618 vs	1593 vs	1423 vs 1123 m	1369 vs	1201 m 1090 vw	1153 w	702 vs	-	-	-	-
BIMD	-	3100-3150	-	1642 s	1618 s	1598 vs	1448 m	-	1222 m	1159 w	-	3040 vw	1605 m	-	-
$[La(BIMD)_3(na)_3]^{+3}$	3358 vs	3195 s	3072 s	1685 m	1618 m	1598 vs	1418 s	1438 s	1226 m	1160 w	836s	3058 w	1618 m	535 m	492 m
$[Ce(BIMD)_3(na)_3]^{+3}$	3372 b	3195 sh	3066 sh	1676 m	1618 s	1608 s	1435 m	1436 s	1236 m	1163 w	834 m	3066 w	1620 m	540 m	460 w
$[Gd(BIMD)_3(na)_3]^{+3}$	3375 s	3187	3060 sh	1688 s	1618 m	160 s	1440 s	1439 s	1232 w	1160 w	832 w	3066 w	1618 m	518 m	480 m
$[Nd(BIMD)_3(na)_3]^{+3}$	3359 vs	3198 s	3068 sh	1670 s	1618 s	1612 s	1435 s	1436 s	1235 m	1176 w	833 m	3068 m	1618 w	545 m	482 w

Table (5) : Bond lengths (A°) for $[M(na)_3(BIMD)_3]^{+3}$ complexes
M : La , Ce , Gd , Nd

C(12),Ce(64) 2.072 C(13),Ce(64) 1.254 C(14),Ce(64) 3.191 N(17),Ce(64) 4.074 C(18),Ce(64) 2.667 O(19),Ce(64) 2.315 N(20),Ce(64) 0.403 H(21),Ce(64) 1.414 H(22),Ce(64) 0.843 O(30),Ce(64) 4.085 Ce(64),H(82) 3.517 Ce(64),H(90) 3.515 Ce(64),H(87) 2.632	C(12),Nd(64) 2.054 C(13),Nd(64) 1.248 C(14),Nd(64) 3.175 N(17),Nd(64) 4.055 C(18),Nd(64) 2.648 O(19),Nd(64) 2.315 N(20),Nd(64) 0.423 H(21),Nd(64) 1.434 H(22),Nd(64) 0.843 O(30),Nd(64) 4.081 Nd(64),H(78) 3.529 Nd(64),H(86) 3.503 Nd(64),H(83) 2.618
C(12),La(64) 2.145 C(13),La(64) 1.282 C(14),La(64) 3.258 C(18),La(64) 2.742 O(19),La(64) 2.315 N(20),La(64) 0.325 H(21),La(64) 1.335 H(22),La(64) 0.850 La(64),H(81) 3.571 La(64),H(89) 3.565 La(64),H(86) 2.691	C(12),Gd(64) 2.000 C(13),Gd(64) 1.231 C(14),Gd(64) 3.125 N(17),Gd(64) 3.996 C(18),Gd(64) 2.592 O(19),Gd(64) 2.317 N(20),Gd(64) 0.482 H(21),Gd(64) 1.493 H(22),Gd(64) 0.845 O(30),Gd(64) 4.071 Gd(64),H(82) 3.484 Gd(64),H(90) 3.466 Gd(64),H(87) 2.575

Table (6) : nemenclature of prepared complexes

Empirical formula	Nomenclature	Abbreviated
La Empirical formula	Trip enzimidazole tris (nicotinamide) Lanthanum (III)	$[La(na)_3(BIMD)_3]^{+3}$
Ce Empirical formula	Trip enzimidazole tris (nicotinamide) Cerium (III)	$[Ce(na)_3(BIMD)_3]^{+3}$
Br Empirical formula	Trip enzimidazole tris (nicotinamide) Gadolgamin (III)	$[Gd(na)_3(BIMD)_3]^{+3}$
Nd Empirical formula	Trip enzimidazole tris (nicotinamide) Neodymum (III)	$[Nd(na)_3(BIMD)_3]^{+3}$

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