Studies on Some Lanthanoid Complexes of Heterocyclic Ligands: Complexes of 2-Pyrazinecarboxamide with Hydrogen-Bonding

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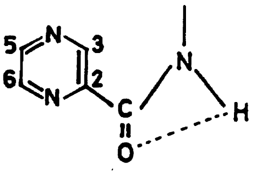
Lanthanoid complexes of 2-pyrazinecarboxamide (PYZA) of the composition, $[LnCl_3(pyza)_3]$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Y), were synthesized and the structures of the isolated complexes studied by elemental analyses, molar conductance, magnetic susceptibility, electronic, FT-IR and multinuclear NMR spectral techniques. Presence of intra- and intermolecular hydrogen bonding in the non-complexed (free state) PYZA and intramolecular hydrogen bonding in the complexed ligand (Ln(III) complex) was indicated by the FT-IR spectra (solution and solid states). Non-coordination through the >C=O and $-NH_2$ groups in the Ln(III) complexes was implied by the FT-IR (solution state) and ^{13}C NMR spectra. The ^{139}La NMR spectrum implied a predominantly ionic bond and low symmetry in the complexes. The hypersensitive band profile of the Nd(III) complex remained uneffected with respect to pH and temperature variations.

2-Pyrazinecarboxamide (PYZA) is a unique antitubercular drug because it is effective in vivo but not in media commonly used to culture tubercle bacilli.[1] Further, the small 2-pyrazinecarboxamide molecule with good lipid solubility was reported to penetrate readily into the central nervous system while rephampacin, the common antitubercular drug, traverses the blood brain barrier with difficulty due perhaps to its bulky size and low water solubility.[2] Referring to the metal complexing ability of PYZA, it can interact with a metal ion in several ways due to its multidentate behavior. Among the metal complexes of PYZA those of copper(II) were extensively studied. Following the crystal structure determination[3] of $[Cu(pyza)_2ClO_4]_n$, the structures of the complexes $[Cu(pyza)_2Cl_2]$, $[Cu(pyza)_2Br_2]$, and $[Cu(pyza)_2(ClO_4)_2]$ originally reported to be square planar and monomeric by Sekizaki and Yamasaki,[4] were reinvestigated by Eckberg and Hatfield[5] based upon low-temperature magnetic moments. The literature on transition metal complexes of PYZA also includes those of Co(II), Ni(II),[6] and Pd(II), Pt(II).[7] No report was made to date on lanthanoid metal complexes of 2-pyrazinecarboxamide. As part of our programme on structural investigations of Ln(III) complexes of N, O-donor ligands,[8—12] we have undertaken synthetic, spectral, and structural studies of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III) complexes of 2-pyrazinecarboxamide (**I**) and the results are reported here (Chart 1).



(**I**)

Chart 1.

Experimental

Preparation and Analyses of Complexes. The trichlorotris(2-pyrazinecarboxamide)lanthanoids, $[LnCl_3(pyza)_3]$, were prepared by mixing together dry ethanol solutions of PYZA (0.37 g in 20 cm^3) and the appropriate metal chloride (0.37 g in 20 cm^3) and refluxing the reaction mixture for 4 h. Addition of ca. 10 cm^3 of acetonitrile to the resulting solution yielded a gummy solid which was macerated in acetonitrile, dissolved in dry ethanol and reprecipitated by adding acetonitrile. Multiple repetitions of this process yielded microcrystalline complexes, which were filtered off and washed several times with a mixture of acetonitrile and ethanol (50 : 50 v/v) and dried in a desiccator at room temperature.

The metal ions, after the decomposition of organic matter with aqua regia followed by treatment with concd H_2SO_4, were estimated volumetrically by EDTA titration,[13] using Xylenol Orange as indicator. Chloride was determined gravimetrically as AgCl. Nitrogen was microanalyzed.

Physical Measurements. Microanalysis was done on a Perkin-Elmer 240 C Analyzer. Molar conductances were measured at room temperature on a WTW conductivity meter. The room temperature magnetic susceptibility measurements were carried out on a Cahn–Faraday electrobalance using $[HgCo(NCS)_4]$ as the calibrant. The FT-IR spectra were recorded on a JASCO FT-IR spectrophotometer model 5300, while the electronic spectra were recorded on Schimadzu UV-vis model-160 and Cray-23 spectrophotometers. The ^{1}H, ^{13}C, and ^{139}La NMR spectra were recorded on a JEOL FX-90Q multinuclear NMR spectrometer.

Results and Discussion

The analytical data given in Table 1 indicate the formation of only one type of complexes, viz., $[LnCl_3(pyza)_3]$, having 1 : 3 metal to ligand stoichiometry which may be represented by the following equation:

$$LnCl_3\cdot nH_2O + 3\ PYZA \xrightarrow[\text{dry EtOH}]{\text{Reflux 4 h}} [LnCl_3(pyza)_3] + nH_2O$$

The colors and melting points of the complexes are in-

Table 1. Analytical Data and General Behavior of PYZA Complexes

Complex	Color	Mp/°C	Analyses[a)]/%			μ_{eff}/B.M.
(Empirical formula)	(yield/%)		Cl	M	N	
[$LaCl_3(pyza)_3$]	Pale yellow	196	16.98	22.39	20.39	Dia
($C_{15}H_{15}N_9O_3Cl_3La$)	(74)		(17.30)	(22.60)	(20.51)	
[$PrCl_3(pyza)_3$]	Pale green	204—206	16.90	22.50	20.26	3.19
($C_{15}H_{15}N_9O_3Cl_3Pr$)	(59)		(17.24)	(22.85)	(20.44)	
[$NdCl_3(pyza)_3$]	Bluish green	212	16.81	22.93	20.52	2.79
($C_{15}H_{15}N_9O_3Cl_3Nd$)	(72)		(17.15)	(23.26)	(20.33)	
[$SmCl_3(pyza)_3$]	Cream	208	16.76	23.97	20.23	1.97
($C_{15}H_{15}N_9O_3Cl_3Sm$)	(64)		(16.98)	(24.01)	(20.13)	
[$EuCl_3(pyza)_3$]	Cream	202	16.67	24.07	19.89	2.92
($C_{15}H_{15}N_9O_3Cl_3Eu$)	(59)		(16.94)	(24.21)	(20.08)	
[$GdCl_3(pyza)_3$]	White	203	16.60	24.61	19.69	7.37
($C_{15}H_{15}N_9O_3Cl_3Gd$)	(76)		(16.80)	(24.84)	(19.91)	
[$TbCl_3(pyza)_3$]	Yellow	190	16.65	24.80	19.70	9.10
($C_{15}H_{15}N_9O_3Cl_3Tb$)	(67)		(16.75)	(25.04)	(19.86)	
[$DyCl_3(pyza)_3$]	Pale yellow	213	16.49	25.02	19.54	11.22
($C_{15}H_{15}N_9O_3Cl_3Dy$)	(61)		(16.66)	(25.46)	(19.75)	
[$YCl_3(pyza)_3$]	Pale yellow	198	18.36	15.55	22.48	Dia
($C_{15}H_{15}N_9O_3Cl_3Y$)	(60)		(18.83)	(15.74)	(22.32)	

a) Required values are given in parentheses.

cluded in Table 1. All the complexes are moderately hygroscopic when exposed to atmosphere and are soluble in water and common organic solvents such as methanol, ethanol, chloroform etc. The molar conductances in methanol solutions (2×10^{-6} mol cm^{-3}) suggest a nonelectrolytic behavior[14)] (19.89 to 26.52 ohm^{-1} cm^2 mol^{-1}).

Magnetic Moments. The room temperature magnetic moments (Table 1) of the present complexes, corrected for diamagnetism show a little deviation from Van-Vleck values.[15)] This deviation may be due to a weak 4f electron participation in bonding with the ligand.

Absorption Spectra. The electronic spectra of the Pr(III), Nd(III), Sm(III), Eu(III), and Dy(III) complexes were recorded in solid state (Nujol mull) as well as in solution (methanol) state and all the spectral bands, the corresponding transitions and the calculated spectral parameters are given in Table 2. The present discussion, however, confines to exclusively the Nd(III) complex as a representative one. The oscillator strengths (P), calculated[18)] from the 2×10^{-3} M solution (1 M=1 mol dm^{-3}) spectrum (MeOH) show an increase in comparison to the aquametal ion which is most likely due to a lowering of molecular symmetry.[19,20)] Further, the spectral features in the hypersensitive band profile of the complex in its solid and solution states remain unaltered indicating a similar environment around the metal ion in both the states. Temperature and pH variations seem to have no effect on the hypersensitive band profile and the oscillator strengths (see foot note of Table 2). Various spectral parameters, viz., $\bar{\beta}$, $b^{1/2}$, $\%\delta$, and η calculated[21—24)] (Table 2) from the solution state absorption spectra suggest a little participation of 4f-electrons in bond formation with PYZA.

Infrared Spectra. The IR spectra of PYZA were recorded in the solid (KBr pellet) as well as solution (chloroform) states and those of the Ln(III) complexes as KBr pellets. The spectral data of the pertinant bands along with the assignments are given in Table 3. The solid state spectrum of PYZA shows doubling of the ν(C=O) and ν(NH) (both symmetric and asymmetric) bands (Table 3) which is most likely due to each of the groups being associated with varying degrees of hydrogen bonding. However, the spectrum in solution (chloroform) state (Fig. 1) shows retention of the doubling features of the symmetric and asymmetric ν(NH) bands and a single sharp band due to ν(C=O). These data may best be interpreted in terms of two types of amide hydrogen atoms, one involving hydrogen bonding (presumably intramolecular type) with the carbonyl oxygen and the other being free. This also supports the coalescence of the two different bands of the carbonyl group of the solid state (presumably on account of intra- and intermolecular hydrogen bondings) into one sharp peak in the solution state (on account of cleavage of the intermolecular hydrogen bonding). A comparison of the solution state spectra of the ligand and the Eu(III) complex (Fig. 1) indicates non-bonding through the $-NH_2$ and >C=O groups on the basis of their stretching frequencies appearing in identical positions. However, the solid state spectra show considerable shifts of the ν(NH) and ν(C=O) frequencies (Table 3) upon complexation, which we are inclined to interpret in terms of varying degrees of hydrogen bonding associated with the carbonyl oxygen and amide hydrogens before and after complexation but not due to coordination through the above groups. The foregoing discussion on NMR spectra provides further support with regards to the non-coordination through the >C=O and the $-NH_2$ goroups.

Table 2. Electronic Spectral Data of Ln(III) Complexs of PYZA

Complex	Band max (cm^{-1})		Assignment	$P\times10^6$	Parameters
	Nujol	MeOH solution			
$[PrCl_3(pyza)_3]$	6340	—	$^3H_4 \rightarrow {}^3F_3$	—	$\bar{\beta}=0.9995$
	6944	—	$\rightarrow {}^3F_4$	—	$b^{1/2}=0.0149$
	9803	—	$\rightarrow {}^1G_4$	—	$\%\delta=0.0448$
	16920	16890$^{a)}$	$\rightarrow {}^1D_2$	9.62	$\eta=0.0025$
	20618	20790	$\rightarrow {}^3P_0$	3.20	
	21230	21276	$\rightarrow {}^3P_1+{}^1I_6$	2.72	
	22392	22420$^{a)}$	$\rightarrow {}^3P_2$	9.53	
$[NdCl_3(pyza)_3]$	11430	11440—11560	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	—	$\bar{\beta}=0.9976$
	12386	12468	$\rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	17.09	$b^{1/2}=0.0346$
	13420	13404	$\rightarrow {}^4F_{7/2}, {}^2S_{3/2}$	15.46	$\%\delta=0.2405$
	14706	14662—15815	$\rightarrow {}^4F_{9/2}, {}^2H_{11/2}$	0.61	$\eta=0.0120$
	17070	17152$^{a)}$	$\rightarrow {}^4G_{5/2}$	27.62	
	18975	19083$^{a)}$	$\rightarrow {}^4G_{7/2}$	0.98	
	—	19530	$\rightarrow {}^4G_{9/2}$	0.14	
	21680	21740	$\rightarrow {}^4G_{11/2}$	—	
	—	23255	$\rightarrow {}^2P_{1/2}$	6.16	
	—	24510	$\rightarrow {}^2D_{5/2}$	—	
$[SmCl_3(pyza)_3]$	6309$^{a)}$	—	$^6H_{5/2} \rightarrow {}^6F_{1/2}$	—	$\bar{\beta}=0.9917$
	6578	—	$\rightarrow {}^6H_{15/2}$	—	$b^{1/2}=0.0642$
	7092	—	$\rightarrow {}^6F_{5/2}$	—	$\%\delta=0.8323$
	7968	—	$\rightarrow {}^6F_{7/2}$	—	$\eta=0.0417$
	9190	9191	$\rightarrow {}^6F_{9/2}$	4.76	
	10471	10362	$\rightarrow {}^4F_{11/2}$	1.02	
	—	18552	$\rightarrow {}^4F_{3/2}$	1.03	
	—	20920	$\rightarrow {}^4I_{11/2}$	1.02	
	—	24875	$\rightarrow {}^4F_{7/2}$	20.77	
$[EuCl_3(pyza)_3]$	17222	17220	$^7F_0 \rightarrow {}^5D_0$	0.22	$\bar{\beta}=0.9909$
	21342	21323$^{a)}$	$\rightarrow {}^5D_2$	1.58	$b^{1/2}=0.0674$
					$\%\delta=0.9183$
					$\eta=0.0458$
$[DyCl_3(pyza)_3]$	—	6557	$^6H_{15/2} \rightarrow {}^6H_{11/2}$	0.82	$\bar{\beta}=0.9762$
	—	7751$^{a)}$	$\rightarrow {}^6H_{9/2}, {}^6F_{11/2}$	1.67	$b^{1/2}=0.1090$
	9086	9090	$\rightarrow {}^6F_{9/2}, {}^6H_{7/2}$	3.16	$\%\delta=2.4380$
	10868	10989	$\rightarrow {}^6F_{7/2}$	3.43	$\eta=0.0121$
	12560	12422	$\rightarrow {}^6F_{5/2}$	2.62	
	13157	13152	$\rightarrow {}^6F_{3/2}$	0.81	
	21163	21276	$\rightarrow {}^4F_{9/2}$	—	
	—	22222	$\rightarrow {}^4I_{15/2}$	—	
	23618	23529	$\rightarrow {}^4G_{11/2}$	—	
	—	25974	$\rightarrow {}^4I_{13/2}$	—	

a) Indicate hypersensitive transitions. b) The oscillator strengths vary in the ranges, 27.62—29.35 and 36.68—37.98 respectively with variation in temperature (29—49 °C) and pH (3.0—6.0).

The considerable shifts, upon complexation in the ring nitrogen band (Table 3) suggest coordination through one of the pyrazine ring nitrogens.[25] The prominent non-ligand bands appearing in the region, 420—418 cm^{-1} may be tentatively assigned to ν(M–N) modes of vibration.[25]

NMR Spectra. PYZA and the Ln(III) complexes (Ln=La and Y) were recorded for ^1H and ^{13}C nuclei while the La(III) complex was also recorded for ^{139}La nucleus.

The ^1H NMR spectral data of the ligand and the complexes (DMSO-d_6 solutions) and the assignments are included in Table 4. The striking feature is that the spectra of the ligand and the complexes show two different $-N\underline{H}_2$ signals indicating nonequivalence of the $-N\underline{H}_2$ protons. Down field shift of the $C_6\underline{H}$ signal ($\delta=0.13$) of the pyrazine moiety in the spectra of the complexes indicates coordination through the ring nitrogen ortho to the amide group. However, the negligible shifts ($\delta=0.06$) of the $-N\underline{H}_2$ signals upon complexation do not substantiate coordination through the amide nitrogen.

The proton decoupled ^{13}C NMR spectra of the ligand

Table 3. IR Spectral Data (cm^{-1}) of Ln(III) Complexes of PYZA

Complex	$\nu(\mathrm{NH})_{\mathrm{asym}}$	$\nu(\mathrm{NH})_{\mathrm{sym}}$	ν(C=O)	Pyrazine ring deformation modes	ν(M–N)
PYZA	3410, 3230	3290, 3165	1720, 1690	665, 435	—
$[\mathrm{LaCl_3(pyza)_3}]$	broad band	broad band	1701, 1676	680, 450	418
$[\mathrm{PrCl_3(pyza)_3}]$	3371, 3220	3280, 3120	1699, 1674	679, 455	420
$[\mathrm{NdCl_3(pyza)_3}]$	3368, 3210	3285, 3123	1701, 1676	675, 451	420
$[\mathrm{SmCl_3(pyza)_3}]$	3368, 3200	3285, 3121	1701, 1676	680, 453	420
$[\mathrm{EuCl_3(pyza)_3}]$	3369, 3220	3280, 3120	1701, 1678	680, 455	420
$[\mathrm{GdCl_3(pyza)_3}]$	3362, 3210	3292, 3123	1701, 1676	680, 455	420
$[\mathrm{TbCl_3(pyza)_3}]$	3373, 3210	3300, 3110	1701, 1678	680, 455	420
$[\mathrm{DyCl_3(pyza)_3}]$	3360, 3220	3285, 3123	1703, 1678	680, 453	420
$[\mathrm{YCl_3(pyza)_3}]$	Broad band	Broad band	1701, 1678	680, 455	418

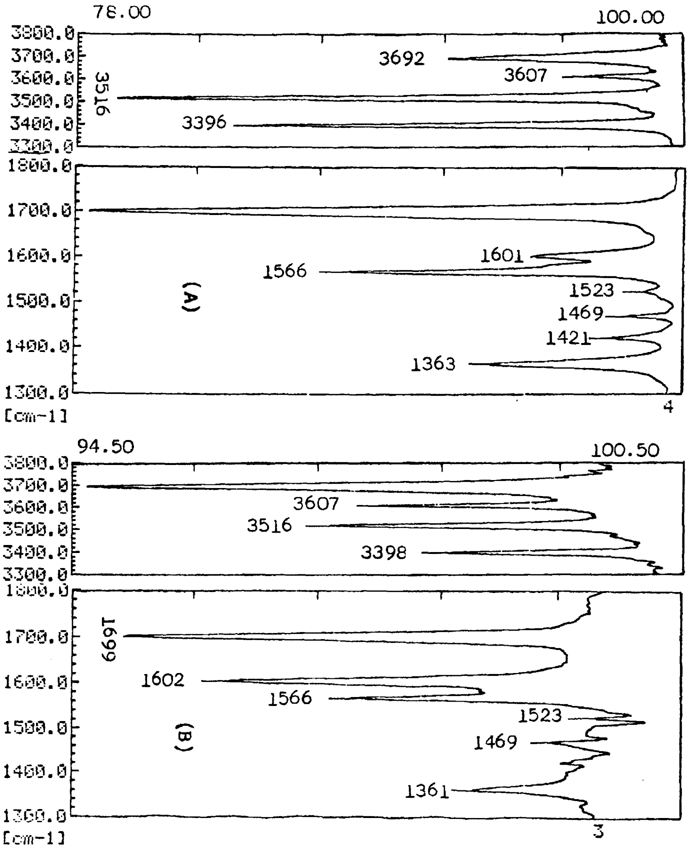


Fig. 1. FT-IR spectra of (A) PYZA and (B) $\mathrm{Eu(pyza)_3Cl_3}$ in chloroform solutions.

and the complexes were recorded in DMSO-d_6 solutions and the spectral data along with the assignments are included in Table 4. The correctness of the ring carbon assignments particulary of $\underline{C}_2$ and $\underline{C}_6$ was confirmed from the proton-coupled ^{13}C NMR spectrum of the ligand. The $\underline{C}_6$ signal is further differentiated from those of $\underline{C}_3$ and $\underline{C}_5$ by the observed shift in the spectra of the complexes. The retention of the >C=O singal precisely at the same position (δ=164.89) in the spectra of the ligand and the complexes suggests non-coordination of the >C=O group. The down field shifts of the $\underline{C}_2$ and $\underline{C}_6$ signals (δ=1.1 and 0.44 respectively) in the spectra of the complexes imply coordination thorugh the ring nitrogen ortho to the amide group.

Spectral evidence towards complex formation was also obtained from ^{139}La NMR spectrum of the La(III) complex recorded in $\mathrm{CD_3OD}$ solution. The signal as expected, appeared as a broad peak ($W_{1/2}$=6800 Hz) centred at $\delta=-210$ with respect to a very dilute aqueous $\mathrm{La(ClO_4)_3}$ solution. The ^{139}La chemical shifts of majority of complexes are reported to fall in the range $\delta=+1090$ to $\delta=-129$ while those of a few complexes fall in the extended range, $\delta=-380$ to -614.[26)] The pronounced high field shift of the present complex is in accordance with the shifts observed for Ln(III) complexes of η^5-cyclopentadienyl ligands.[26,27)] as well as for those of η^6-arene[28)] ligands. Since the ^{139}La chemical shifts seem to follow the so called 'inverse order', the

Table 4. ^1H and ^{13}C NMR Spectral Data[a)]

Protons/ carbons	PYZA	$[LaCl_3(pyza)_3]$	$[YCl_3(pyza)_3]$
$-N\underline{H}_2$	8.20, 7.80	8.23, 7.86	8.26, 7.85
$C_3\underline{H}$	9.10	9.06	9.06
$C_5\underline{H}$	8.73^d	8.76^s	8.76^s
$C_6\underline{H}$	8.60^d	8.73^s	8.81^s
$>\underline{C}=O$	164.89	164.85	164.89
C_2	151.55	152.65	152.65
C_3	147.55	147.55	147.53
C_5	143.55	143.55	143.55
C_6	139.55	139.99	139.99

s=singlet, d=doublet.
a) ^{13}C NMR spectra measured in ppm with respect to DMSO-d_6 (δ=39.50).

high-field chemical shift of the present complex is suggestive of its hightly ionic nature. The half width, $W_{1/2}$, of ^{139}La resonance signal is known to be very sensitive to changes in the symmetry and electronic field gradient of the ligand sphere. The large line width of the present complex, 6800 Hz, arising from a rapid quadrapolar relaxation, is close to that of $[La(thf)_4][(C_5H_5)_3La(n\text{-}C_4H_9)]$[26)] indicating low symmetry around the metal ion.

Conclusion

The ligand, 2-pyrazinecarboxamide as well as the Ln(III) complexes of the empirical formula, $Ln(pyza)_3Cl_3$, seem to involve inter- and/or intramolecular hydrogen bonding between the carbonyl oxygen and amide hydrogens in solid state and the intermolecular hydrogen bonding, vide the FT-IR spectra, seems to be broken in very dilute chloroform solutions. A metal-dependent coordinating behavior of PYZA may be visualized from the fact that the ligand coordinates through, apart from the ring nitrogen ortho to the amide group (present study), the carbonyl oxygen with copper(II) (vide single crystal study[3)]). ^{13}C NMR and FT-IR ($CHCl_3$ solution) spectra provide convincing support to rule out the >C=O and $-NH_2$ groups coordination in the present complexes. A unidentate bonding behavior of the heterocyclic amide (PYZA) with three potential donor sites seems to be obviously surprizing but the spectral data (IR and NMR) provide with the convincing experimental evidence to rule out coordination through both the carbonyl and amide groups. Strong intramolecular hydrogen bonding between the two groups both in the solid and solution states apparently precludes them from coordinating to the Ln(III) ion. However, a single crystal X-ray study can only establish the bonding sites beyond any doubt.

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