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Synthesis, Physical Properties, and Spectroscopy of 2,3-Quinoxalinedicarboxamide Complexes

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New complexes of the general formulae $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Y}$; Qxda = 2,3-quinoxalinedicarboxamide) and $[\text{Ln}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$ ($\text{Ln} = \text{Y}, \text{La}$) have been synthesized and characterized by elemental analyses, conductivity measurements, thermal (TG, DTG, DTA) method, and spectral (IR and UV—VIS) studies. All the data are discussed in terms of the nature of bonding and the possible structural types. It has been found that coordination takes place through both oxygen atoms of the amide group and two types of species, mononuclear and linear homopolynuclear, are formed.

Heterocyclic carboxamides are known to possess powerful antitubercular activity [1]. Further, the metal complexes of ligands that have biological activity are more active than the free ligands [2, 3]. In view of this, metal complexes with several ligands of this type, e.g. 2-pyrazinecarboxamide [4, 5], 2,3-pyrazinedicarboxamide [5, 6], *N,N,N',N'*-tetramethyl-2,6-pyridinedicarboxamide [7], and 2-quinoxalinecarboxamide [8] have been studied and different coordination models proposed. However, complexes of 2,3-quinoxalinedicarboxamide with some metals of group IIIb have not been reported so far. The present study describes the synthesis and characterization of some of these complexes.

EXPERIMENTAL

2,3-Quinoxalinedicarboxamide (Qxda) was prepared according to the literature method [9]. Lanthanide(III) chlorides were prepared from their oxides by treatment with hydrochloric acid.

IR spectra were taken on a NIC-5DX spectrophotometer (KBr disks) in the range of $\tilde{\nu} = 200\text{—}4000\text{ cm}^{-1}$. UV spectra (in solution) were recorded in the $\lambda = 200\text{—}500\text{ nm}$ region using a spectrophotometer 240 (Shimadzu, Japan). Molar conductivity measurement were made with a DDS-IIA conductometer with dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as solvents, separately, at 25 °C. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out by a TG—DTA meter (Thermoflex) in a nitrogen atmosphere between room temperature and 800 °C.

Lanthanide Complexes

The complexes $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ were prepared by mixing hydrous lanthanide(III) chloride (1 mmol) in 20 cm³ of ethanol and Qxda (2 mmol) in 20 cm³ of dioxane and refluxing the solution for 10 h. The mixture was then concentrated to the appropriate volume. The solid, which

Table 1. Characterization of the Complexes Prepared

Complex	Ln	w _i (calc.)/% w _i (found)/%					Colour
		C	H	N	Cl	Ln	
I	La	22.85	3.07	10.7	20.24	36.41	yellow
		22.82	2.99	10.4	20.19	26.38	
II	Pr	22.77	3.06	10.6	20.16	26.71	black
		22.76	3.01	10.4	20.14	26.64	
III	Y	25.26	3.39	11.79	22.37	18.70	yellow-green
		25.18	3.32	11.76	22.37	18.66	
IV	La ₃	22.93	8.23	2.94	23.48	30.63	reddish
		22.98	8.16	2.88	23.39	30.48	
V	Y ₃	25.79	9.25	3.30	26.39	22.03	yellow-green
		25.74	9.21	3.27	26.38	22.06	

formed when the mixture was cooled, was filtered, washed several times with anhydrous ethanol—ether and dried at 80 °C.

The complexes $[\text{Ln}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$ were prepared by refluxing a mixture of some of hydrous metal (group IIIb) chloride in ethanol and the ligand in dioxane in a mole ratio 1 : 1 for 10 h. The solid, which formed when the mixture cooled, was collected and washed with anhydrous ethanol—ether. The prepared complexes are listed and characterized in Table 1.

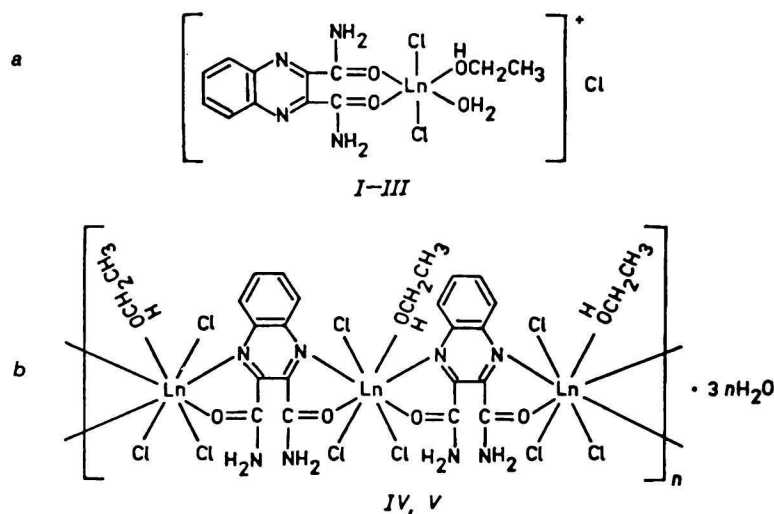
RESULTS AND DISCUSSION

Complexes of 2,3-quinoxalinedicarboxamide with some of lanthanide metals are powder and insoluble in water and common organic solvent, but soluble in DMF and DMSO. It has been found by elemental analyses that $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ form complexes without loss of chloride ions of the general formula $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ and $[\text{Ln}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$. The measurements of molar conductivity, IR and UV spectra, TG and DTA suggest the structure shown in Fig. 1.

The IR wavenumbers along with their relative assignments are given in Table 2. 2,3-Quinoxalinedicarboxamide exhibits bands of $\nu_{\text{as}}(\text{OCN})$ vibrations at $\tilde{\nu} = 1680$ and 1692 cm^{-1} and of $\nu_{\text{s}}(\text{OCN})$ at $\tilde{\nu} = 1348$ and 1393 cm^{-1} . The mononuclear complexes $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ reveal large positive and negative shifts (19–20 cm^{-1}) in the symmetric and antisymmetric $\nu(\text{OCN})$ modes, respectively indicating that the oxygen atom of the amide group is involved in coordination to the metal. Again the band corresponding to quinoxaline ring out-of-plane bending vibrations (at $\tilde{\nu} \approx 485 \text{ cm}^{-1}$) remains almost unshifted relative to the free ligand (487 cm^{-1}) indicating uncoordination of ring nitrogen to the metal. However, the presence of

Table 2. Important IR Spectral Data ($\tilde{\nu}/\text{cm}^{-1}$) of the Ligand and Complexes

Compound	$\nu(\text{NH}_2)$	$\nu_{\text{s}}(\text{OCN})$	$\nu_{\text{as}}(\text{OCN})$	$\nu(\text{Qxda})$	$\nu(\text{C}=\text{O})$	$\nu(\text{Ln}—\text{O})$	$\nu(\text{Ln}—\text{N})$	$\nu(\text{Ln}—\text{Cl})$
Qxda	3428	1680	1348	485	1064	—	—	—
	3140	1692	1393					
I	3404 br	1692	1401	486	1034	460		279
II	3496 br	1660	1405	489	1030	458		255
III	3394 br	1662	1404	487	1024	456		253
IV	3394 br	1657	1393	512	1028	461	320	271
V	3395 br	1653	1396	520	1030	455	309	268

**Fig. 1.** Proposed structure for the complexes a) $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$, b) $[\text{Ln}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$.

the band at $\tilde{\nu} \approx 885 \text{ cm}^{-1}$ confirms the existence of coordinated water in the complexes.

In the homopolynuclear complexes $[\text{Ln}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$ larger positive and negative shifts ($23\text{--}27 \text{ cm}^{-1}$) in the symmetric and anti-symmetric $\nu(\text{OCN})$ vibrations can be observed and the band of the quinoxaline ring out-of-plane bending vibrations is shifted to higher wavenumber at ca. 512 cm^{-1} indicating coordination of amide oxygen and ring nitrogen to the metals.

Moreover, in both types of complexes, mononuclear and homopolynuclear, presence of the bands at $\tilde{\nu} = 3260, 1469, 1036$, and 861 cm^{-1} can be due to the coordinated ethanol molecules and a broad $\nu(\text{OH})$ band around $3000\text{--}3500 \text{ cm}^{-1}$ which overlaps all NH_2 bands [10–15].

Studies on the FIR spectra of these complexes were also made. The absorption peaks at $\tilde{\nu} = 460$ and 345 cm^{-1} are assigned to the $\nu(\text{Ln—O})$ vibrations, the $\nu(\text{Ln—N})$ band appeared at 280 cm^{-1} and the band at 246 cm^{-1} may be attributed to the $\nu(\text{Ln—Cl})$ vibrations.

UV–VIS absorption spectra of the ligand and complexes in DMSO are shown in Table 3. From the UV spectra of these complexes it is evident that the K band ($\pi \rightarrow \pi^*$ transition) of the ligand at 328 nm is shifted to lower wavelength of 318–324 nm and the band at 262 nm is shifted to 254–257 nm. It is quite possible that the central ion is coordinated with ligand to cause an increase in conjugation in the complexes and a decrease in $\pi \rightarrow \pi^*$ transition energy. Thus, these small changes in the wavelength of these complexes as compared to that of the parent ligand suggest that the metal ions are bonded to the Qxda entity.

The molar electrolytic conductivities of the complexes $[\text{Ln}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ in DMF and DMSO, respectively, are reported in Table 4. Lower molar conductivities for the complexes $[\text{Ln}_3(\text{Qxda})_2$

Table 3. UV Spectral Data of the Ligand and Complexes

Compound	$c \cdot 10^4 / (\text{mol dm}^{-3})$	$\lambda_{\text{max}} / \text{nm} (\epsilon_{\text{max}} / (\text{m}^2 \text{mol}^{-1}))$
Qxda	0.45	328 (200), 262 (142)
I	0.30	324 (286), 257 (186)
II	0.25	322 (294), 256 (316)
III	0.50	320 (178), 256 (110)
IV	0.50	318 (180), 254 (124)

Table 4. Molar Conductivities of the Complexes at 25 °C

Complex	Dimethylformamide		Dimethyl sulfoxide	
	$c \cdot 10^3 / \text{mol dm}^{-3}$	$\lambda / \text{S cm}^2 \text{mol}^{-1}$	$c \cdot 10^3 / \text{mol dm}^{-3}$	$\lambda / \text{S cm}^2 \text{mol}^{-1}$
I	1.03	55.8	1.12	65.0
II	1.11	54.2	1.01	58.9
III	1.08	56.1	1.04	53.3
IV	1.01	34.1	0.98	33.6
V	0.98	32.5	1.06	31.8

$\cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$ indicated that the ionization ability of the complexes in DMF and DMSO was weak due to the polymer coordination sphere and the complexes may be nonelectrolytes [16].

In order to investigate thermal properties we measured mass loss and decomposition temperature of the ligand and two complexes $[\text{Y}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$ and $[\text{La}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$ by the TG and DTA methods (Fig. 2). The TG–DTA diagram of the ligand (Fig. 2a) shows that the ligand begins to decompose at 282°C endothermically and lose about 15.0 % of its mass, which corresponds to the loss of two $-\text{NH}_2$ groups (calculated value 14.8 %). It then loses ca. 49.9 % of its mass at 363°C , perhaps indicating that the group of $[\text{C}_4\text{N}_2\text{O}_2]$ breaks away from the phenyl ring (calculated value 50.0 %), and the rest loss of mass about 35.6 % can be observed at 492°C (calculated value 35.2 %).

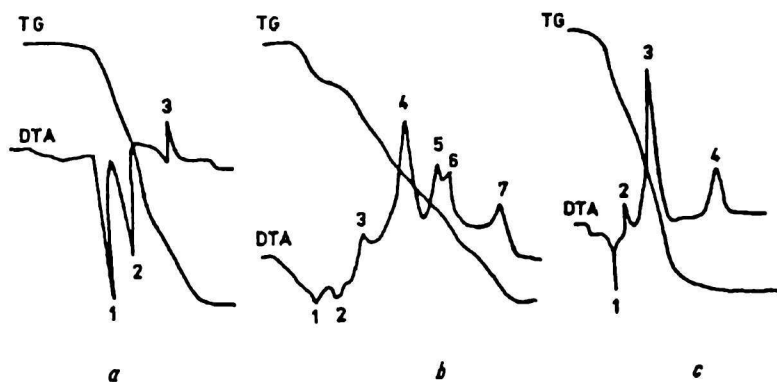


Fig. 2 TG–DTA diagram of: a) Qxda, b) $[\text{Y}(\text{Qxda}) \cdot \text{Cl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot \text{H}_2\text{O}]$, c) $[\text{La}_3(\text{Qxda})_2 \cdot 3\text{Cl}_3 \cdot 3\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}]$. $\theta/^\circ\text{C}$: a) 1. 282, 2. 363, 3. 492; b) 1. 117, 2. 207, 3. 286, 4. 457, 5. 545, 6. 578, 7. 682; c) 1. 90, 2. 200, 3. 488, 4. 564.

The TG—DTA diagram of the complex $[Y(Qxda) \cdot Cl_3 \cdot C_2H_6O \cdot H_2O]$ (Fig. 2b) indicates that this complex loses about 4.0 % of its mass at 117 °C, which corresponds to the loss of one molecule of coordinated water (calculated value 3.8 %). It then loses ca. 9.8 % of its mass at 207 °C, perhaps indicating that one molecule of coordinated ethanol is lost (calculated value 9.7 %). The complex decomposes exothermically and continuously at 286, 457, 545, 578, and 682 °C. The TG—DTA diagram of the complex $[La_3(Qxda)_2 \cdot 3Cl_3 \cdot 3C_2H_6O \cdot 3H_2O]$ (Fig. 2c) indicates that the complex loses 4.0 % of its mass at 90 °C. This should be due to the release of its three molecules of crystal water (calculated value equals 3.97 %). The three molecules of coordinated ethanol are lost endothermically at 200 °C (found mass loss 10.6 %, calculated 10.2 %). The complex continuously decomposes endothermically at 200, 488, and 564 °C. Decomposition is finally complete at 680 °C and oxide of the residue is formed.

It can be seen from the aforementioned data that two types of complexes are formed. The coordination numbers of the central ions are different, *i.e.* those of $[Ln(Qxda) \cdot Cl_3 \cdot C_2H_6O \cdot H_2O]$ and $[Ln_3(Qxda)_2 \cdot 3Cl_3 \cdot 3C_2H_6O \cdot 3H_2O]$ equal six and eight, respectively.

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