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Khimiya Geterotsiklicheskikh Soedinenii, Vo. 2, No. 5, pp. 729-733, 1966

New complex compounds of some rare earths (samarium, europium, gadolinium, dysprosium and ytterbium) with the bidentate ligand pyridine-2-aldoxime have been prepared. Their absorption spectrum in the ultra-violet, visible and infrared regions have been recorded.

Introduction

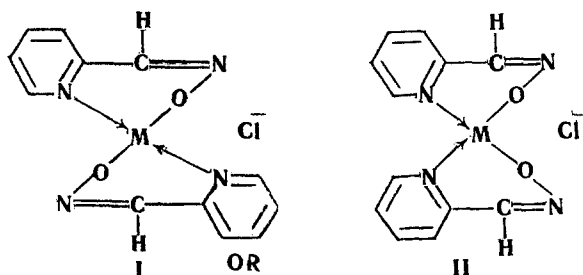
Rare earth complexes have received considerable attention because of their possible application to lasers[1]. Much work has been done on the rare earth complexes on systems containing oxygen donors [2]. Recently complexes with systems containing nitrogen donors [3] have been prepared and found to fluoresce in the visible region. With the goal of investigating the fluorescence properties of rare earth complexes with more systems containing both oxygen and nitrogen donors, pyridine-2-aldoxime has been chosen, as it has been pointed out by Krause and Busch [4] that the complexing properties of pyridine-2-aldoxime would be expected to follow from those of 2, 2'-bipyridine and dimethylglyoxime, since pyridine-2-aldoxime incorporates in its structure the functional groups of both bipyridine and dimethylglyoxime.

Table 1

Metal	pH	Mp or decomposition point °C	Color	% of Nitrogen		% of Chlorine	
				Calc.*	Found	Calc.*	Found
Sm	6.5	230	Lilac	13.09	12.91	8.29	8.9
Eu	6.5	215-216	Reddish brown	13.04	14.2	8.26	9.0
Gd	6.5	185-186	Buff	12.88	13.8	8.16	9.1
Dy	5.8	213-214	Pale lilac	12.71	13.7	8.06	8.9
Ib	6.2	280	Pink	12.43	13.2	7.88	8.3

*Calculated for $\text{Ln}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2\text{Cl}$.

Complexes of copper (II) were prepared [5] in which it was shown that pyridine-2-aldoxime could behave as a bidentate ligand either with or without the loss of oxime protons. Complexes of nickel (II), palladium(II), and platinum (II), were also prepared [6], characterized, and compared with complexes formed by similar ligands (dimethylglyoxime,



2, 2'-bipyridine, 2-methyl-2-amino-3-butanone oxime). In a study of copper (II), platinum(II), and palladium(II) pyridine-2-aldoxime complexes [7] it was suggested that pyridine-2-aldoxime is an unsymmetrical chelating agent. In a 2:1 complex the four nitrogen atoms were arranged in a square-planar fashion and the complex may either assume the cis or trans configuration. In the cis configuration the oxime groups are arranged much as they are in dimethylglyoxime complexes. It seems that in this case intramolecular hydrogen bonding may occur to form a pseudo six-membered ring system and further stabilize the complex.

Experimental

Equipment and materials. The absorption spectra in the ultraviolet and visible region were recorded with a Hilger-Watts spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer model 137 infracord. The compounds were examined as Nujol mulls.

Spectrographically pure rare earth oxides (99.9%) of the individual rare earth elements were obtained from Johnson, Matthey Ltd., London.

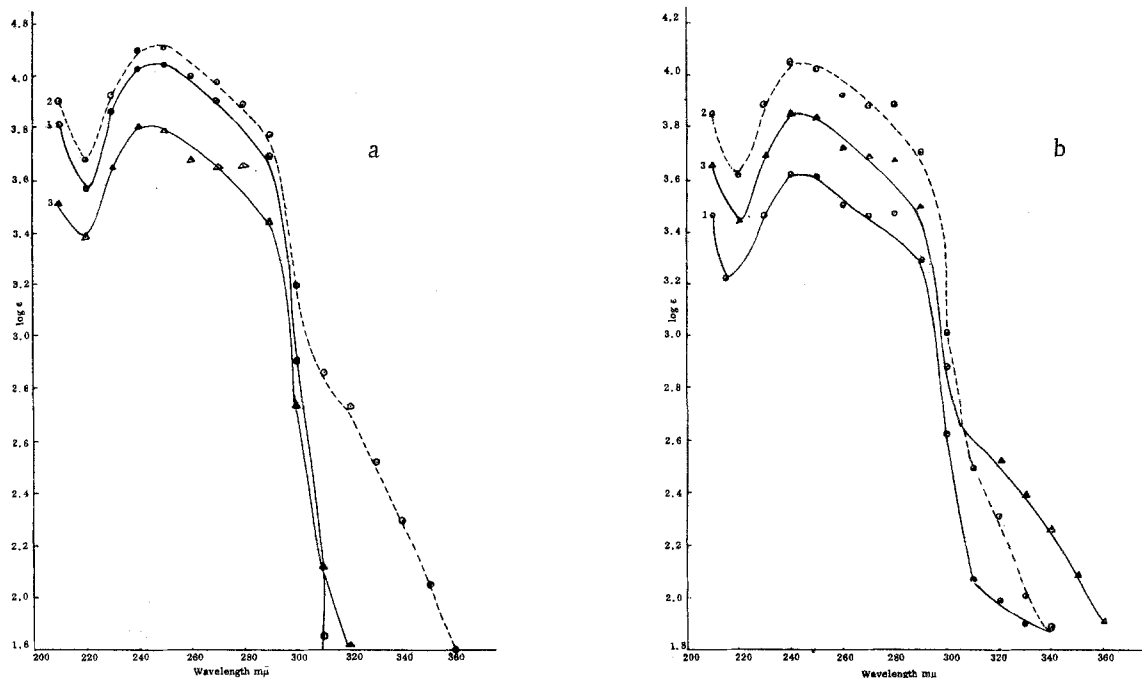


Fig. 2. Solvent used—methanol: a) curve 1 pyridine-2-aldoxime, curve 2 samarium chelate, curve 3 europium chelate; b) curve 1 gadolinium chelate, curve 2 dysprosium chelate, curve 3 ytterbium chelate.

The organic solvents employed were of reagent quality and were dried before use.

Pyridine-2-aldoxime was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A. It was used without further purification.

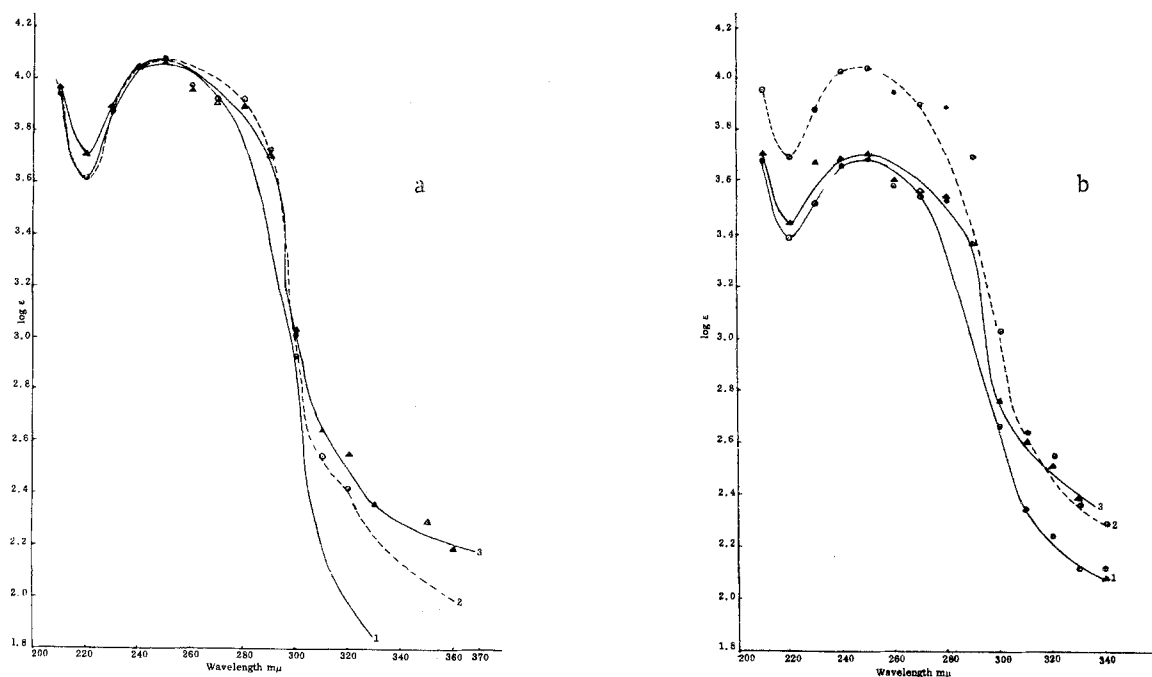


Fig. 3. Solvent used—ethanol: a) curve 1 pyridine-2-aldoxime, curve 2 samarium chelate, curve 3 europium chelate; b) curve 1 gadolinium chelate, curve 2 dysprosium chelate, curve 3 ytterbium chelate.

Preparation of the chelates. A weighed amount of the oxide sample was dissolved in A. R. grade hydrochloric acid and the resulting chloride solution was carefully evaporated to dryness on a steam bath to remove the acid. The residue was dissolved in 20 ml of absolute alcohol, a calculated amount of the ligand (mole ratio 1:3) in 30 ml of ethanol was

Infrared Absorption Bands of Pyridine-2-Aldoxime and Several Rare Earth Chelates.

sh: shoulder, sm: sharp medium, lm: low medium, ss: strong sharp, sl: sharp low, sp: sharp broad,
b: broad, m: medium,

added, and the pH of the solution adjusted to the optimum value by addition of alcoholic ammonia. The solution was slowly concentrated on a steam bath until the solid complex separated. The solution was filtered, washed with benzene to remove excess ligand, purified of ethanol, and vacuum dried. It was shown (a weighed amount of the dried chelate was ignited in a platinum crucible and the residual oxide weighed) that the metal to ligand ratio is 1:2. The physical properties of the chelates, along with the elemental analysis are summarized in Table I. The probable configuration of the chelates is represented in Fig. 1.

Spectral Data

Ultraviolet region. The rare earth complexes in the 200–360 m μ region are subject to the following limitations: (i) the slightly soluble nature of the complexes in solvents transparent to this region, (ii) the relatively high absorption of the ligand compared to the metal ion. Investigations in this region were therefore confined to methanol and ethanol. The absorptivity of the ligand masks any structure or splitting developed by metal ions and one can look for wavelength shifts in the absorption bands associated with the ligand. The ligand and the chelates show only one absorption maximum on the solvents employed. In methanol the ligand has an absorption maximum at 240 m μ ($\log \epsilon = 4.03$). In the europium ($\log \epsilon = 3.8$), gadolinium ($\log \epsilon = 3.61$), dysprosium ($\log \epsilon = 4.03$), and ytterbium ($\log \epsilon = 3.84$) chelates there is a shift of the absorption maxima to the blue end of the spectrum. In ethanol both the ligand and the chelates exhibit a maximum absorption curves of the ligand and the several rare earth chelates in both the solvents employed.

Visible region. Sm³⁺, Eu³⁺, Dy³⁺ and Yb³⁺ have characteristic absorption maxima at 402, 395, 910, and 975 m μ , respectively. In the chelates the characteristic absorption maxima of the respective elements could not be located.

Infrared region (2–15 μ). The infrared absorption bands of pyridine-2-aldoxime and its metal complexes were recorded [8] and assignments for C=N, N–O stretching and four pyridine ring bands were assigned for the complexes we investigated. The 2-substituted pyridine ring should be responsible for four ring stretching frequencies [9] between 1620 and 1425 cm⁻¹. Normal oximes [10, 11] have bands at 3300–3150 cm⁻¹ (O–H stretch), 1690–1620 cm⁻¹ (C=N stretch), and a band near 950 cm⁻¹ (N–O stretch). In the present investigations four ring stretching frequencies have been located in the ligand and in the chelates between 1630–1400 cm⁻¹. A fifth band located near 1500 cm⁻¹ in all the chelates and the ligand could be assigned to the C=N vibrational frequency. The N–O stretch frequency normally located in oximes around 955 cm⁻¹ could, however, be located with sharp medium intensity in the ligand. In all the chelates there is broad band between 965–950 cm⁻¹ which could be assigned to the N–O stretch frequency. The band located around 3250 cm⁻¹ in the ligand and the chelates is due to the O–H stretch frequency. Table II summarizes the absorption bands of the ligand and several rare earth chelates with probable assignments.

The authors are grateful to the authorities of the Osmania University and to Prof. N. V. Subba Rao for his keen interest and encouragement. The authors are grateful to Prof. A. N. Kost, Visiting Professor, for his valuable suggestions concerning this publication. One of the authors (V.R.R.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for financial assistance.

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