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Lanthanide Complexes with Acetylacetone and 5- (4-Nitrophenyl) -10, 15, 20-Triphenylporphyrin Ligands

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Abstract: Five lanthanide porphyrin complexes with 5- (4-nitrophenyl) -10, 15, 20-triphenyl porphyrin and acetylacetonate ligands were synthesized and characterized by elemental analysis, IR spectra, Uv-visible spectra, ^{1}H NMR. The structures of the complexes were proposed.

Keywords: lanthanide ion; porphyrin; complexes.

Since the first lanthanide porphyrin was synthesized in 1974[1], a number of this class of porphyrins have been synthesized[2]. Because lanthanide ion has special electron structure, people are interested in properties of lanthanide porphyrin complexes such as catalytic function, optical storage, *etc*[3]. In general, more symmetrically functional lanthanide porphyrins have been studied, but fewer unsymmetrical lanthanide porphyrins are reported.

Now lanthanide complexes of unsymmetrically meso-substituted phenyl porphyrin acetylacetonate 5- (4-nitrophenyl) -10, 15, 20 - triphenylporphyrin LnNTpp (acac), where Ln = Tb, Gd, Er, Yb; N = 4-nitrophenyl; Tpp = triphenylporphyrin; acac = acetylacetone, have been prepared and characterized.

5, 10, 15, 20-tetraphenylporphyrin (1.0 g) was dissolved in chloroform (150 ml) and stirred. Fuming nitric acid (1.7 g) was added dropwise at room temperature for 1 h period. The dark green solution was extracted with 6×200 ml water and dried over magnesium sulfate, sodium carbonate. The solution was concentrated to 50 ml and was applied to a neutral alumina and eluted with chloroform[5], giving mono (nitrophenyl) triphenyl porphyrin in 80% yield.

5 - (4 - nitrophenyl) - 10, 15, 20 - triphenyl porphyrin (H_2NTpp) (0.3 g) and hydrated tris (2, 4-pentanedionato) lanthanide [(Ln (acac) $_3$ • $3H_2O$, Ln = Tb, Gd, Er, Yb)] (0.6 g) were refluxed in 1, 2, 4-trichlorobenzene (40 ml) under dry nitrogen for about 3 h. The reaction mixture was chromatographed on neutral alumina column. The first band eluted by chloroform was the ligand. Then the second band eluted by dimethylsulphoxide (DMSO) was the complexes. The same volume chloroform was added into the DMSO solution and extracted with water for three times. The chloroform layer was condensed and evaporated to dryness. The yield was 0.2 g.

Elemental analysis show the composition of the complexes is $LnC_{49}H_{34}N_5O_4$.

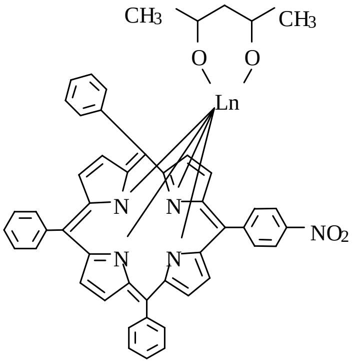
Infrared spectra: the band at 3322cm^{-1} in the free base H_2N Tpp is due to the N-H stretching vibration of the porphyrin core. But the band in the complexes disappears since the hydrogen atom in N-H bonding is replaced by the lanthanide ion. The broad band at 1520 cm^{-1} is due to N-O stretching vibration. It slightly changes in the complexes. The band at 359~374 cm^{-1} is assigned to the Ln-O stretching vibration[6]. The appearance of

Ln-O band and C-H band of the acetylacetone indicates the acetylacetone ring is coordinated to the lanthanide ion.

Uv-visible spectra: the visible absorption bands of the free base H_2NTpp appear at 419 (Soret), 515, 555, 595, 644 nm and those of the complexes are near 424 (Soret), 516, 553, 593 nm. The Soret band is shifted to 424 nm in the complexes. The band at 644 nm disappears in the complexes. Compared to the absorption band of the LnTPP (acac)[6], which appears at 421 nm (Soret), 514, 553, 594 nm, LnNTpp (acac) only take a small change when one meso-phenyl is replaced by a p-nitro phenyl group.

NMR spectra: ($CDCl_3$) for LnNTpp (acac) are at 2.38 (CH_3 of acetylacetonate), 8.962, 8.873~8.861 (β-pyrrole), 8.231 (nitro-phenyl), 7.76~7.165 (phenyl). Compared to ^{1}H NMR signal for the free base[5], the complex is different from the free base at two points: First, -2.74 ppm of the free base porphyrin disappears as the hydrogen atom in the N-H bond is replaced by the lanthanide ion. Second, 2.38 ppm of the LnNTpp (acac) appears due to the methyl groups of the acetylacetonate ring. This indicates that the acetylacetonate ring is coordinated to the lanthanide ion.

From the above results, we can propose the structure of the LnNTpp (acac) which is shown in the figure.



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