Luminescence properties of isomeric lanthanide pyridine-carboxylates and pyridine-dicarboxylates

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The application of dipicolinic acid as a basic element of a self-assembly triple helical structures (helicates), use of picolinate in organic light emitting diodes (OLEDs), and investigations of insulin-mimetic properties of vanadium and zinc picolinates have stimulated our interest to the spectroscopy of the lanthanide pyridine-carboxylates and pyridine-dicarboxylates.

Lanthanide complexes with isomeric pyridine-carboxylic acids of formula $Ln(L)_3.2H_2O$ (where Ln is Eu, Tb, Gd, Dy and L is 2-, 3-, 4-pyridine-carboxylic acids) and two families of the compounds of six pyridine-dicarboxylic acids (2,6-, 2,5-, 2,4-, 2,3-, 3,4-, 3,5-pyridine-dicarboxylic acids) of content $Na_3Ln(L)_3.nH_2O$ and $HLn(L)_2.mH_2O$, where L is corresponding deprotonated acid were synthesised and characterised by elemental analysis.

Luminescence excitation, luminescence, vibration Raman and IR spectra of these compounds were studied. Different temperature dependence of the luminescence spectra in the case europium pyridine-carboxylates (Fig. 1, 2) have been attributed to the relative freedom of carboxyl group orientation in cases of nicotinate and isonicotinate and presence of the chelate cycles in the structure of the picolinate.

Bands of terbium f-d transitions, intraligand charge transfer and ligand-to-Eu^{3+} charge transfer bands have been identified by comparison of the luminescence excitation spectra of europium and terbium salts. For example, high-frequency band of ligand in spectrum of terbium picolinate differs from the same band in spectra of europium salts by presence of a “shoulder” or some slight band (low frequency edge at 30000 cm^{-1}, maximum at 33000 cm^{-1}). This band can be assigned to the f-d transition of Tb^{3+}. The similar picture was observed in the luminescence excitation spectrum of terbium dipicolinate.

It is found that position of carboxyl group in relation to the nitrogen heteroatom of the pyridine ring determines the frequency of the intraligand charge transfer band in europium pyridine-carboxylate spectra. The frequency of this band is maximum at orto-position of carboxyl group (picolinate) and is minimum at para-position of carboxyl group (isonicotinate).

The europium salt of isonicotinic acid has low value of luminance (ratio of $^5D_0$-$^7F_2$ transition intensity to $^5D_0$-$^7F_1$ transition intensity is equal to 4) but presence of most low-frequency band of intraligand charge transfer can promote use of this compound in OLEDs as the layer with electronic conductivity.

Summarizing data obtained and our earlier experimental investigations on spectroscopy of europium β-diketonates we conclude that for increase of the luminescence quantum yield of lanthanide complexes it is necessary to introduce in their content the ligands with high values of optical electronegativity and low values of polarizability.

Possible mechanisms of the excitation energy decay as well as mechanisms of energy transfer from the ligands to the lanthanide ions are discussed.

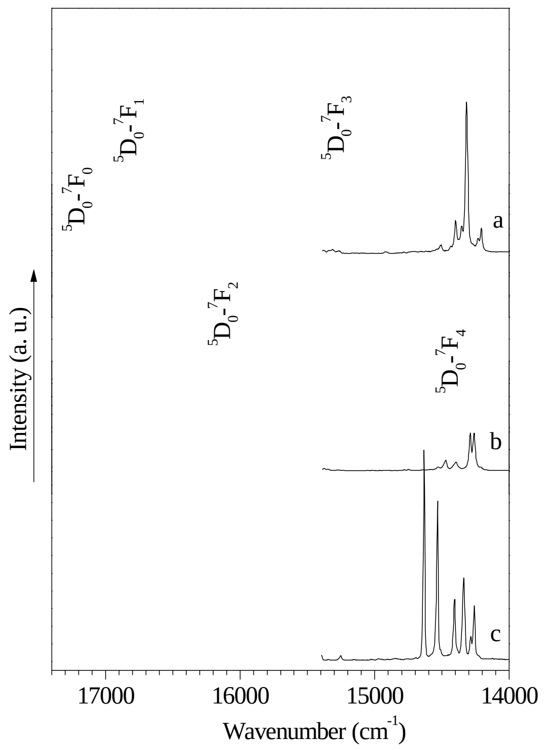

Fig. 1. Luminescence spectra of $Eu(isonic)_3.2H_2O$ (a), $Eu(nic)_3.2H_2O$ (b), $Eu(pic)_3.2H_2O$ (c) at 77 K

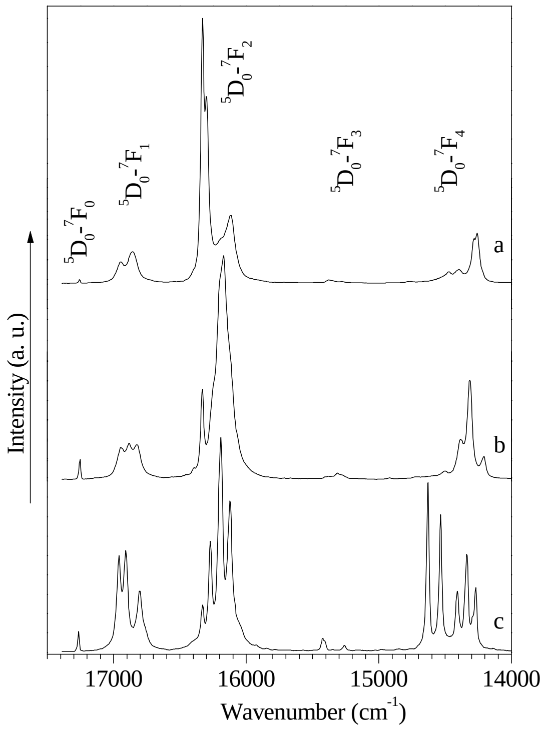

Fig. 2. Luminescence spectra of $Eu(isonic)_3.2H_2O$ (a), $Eu(nic)_3.2H_2O$ (b) and $Eu(pic)_3.2H_2O$ (c) at 300 K

Information on the details of the structure of lanthanide pyridine-carboxylates and pyridine-dicarboxylates has been obtained. The increase in the carboxyl groups polarizability observed in Raman spectra of lanthanide cinchomeronates is due to the turn of these groups out of plane of the pyridine ring that promotes the ligand-europium charge transfer.

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