It was found that the intensity of hypersensitive bands is closely related to the refractivity of solvent. A possible mechanism of solvent effect on intensities of f–f transition is discussed within the framework of the Mason's polarizability mechanism.

Effect of solvent on fluorescence properties of Eu(III) was investigated and mechanism of fluorescence quenching is proposed.

B20

Application of the Luminescence and Absorption Spectroscopy and the X-ray Method to the Study of Ln^{3+} Ions Interactions with Aminoacids

J. LEGENDZIEWICZ, E. HUSKOWSKA

Institute of Chemistry, University of Wrocław, Poland

G. ARGAY

Central Research Institute for Chemistry of Hungarian Academy of Sciences, Budapest, Hungary

and A. WAŚKOWSKA

Institute for Low Temperature and Structure Research Polish Academy of Sciences, Wrocław, Poland.

The Nd^{3+}, Ho^{3+} and Eu^{3+} complexes with glycine, alanine and glutamic acid were synthetized and obtained in a form of monocrystals. Absorption and luminescence spectra recorded in the region of 8000–35000 cm^{-1} were measured along the crystallographic axes. Intensities of the f–f transitions were analysed on the base of Judd theory. The X-ray crystal structure determination of the $Nd(gly)_3(ClO_4)_34\cdot5H_2O$ is reported. Crystals are triclinic, space group $P\bar{1}$, with a = 11.554(4) Å, b = 14.108(1) Å, c = 15.660(3) Å, α = 97.11(1)°, β = 102.82(2)°, γ = 105.20(2)°, V = 2355.25 Å^3, Z = 4, *M.W.* = 747.7, D_c = 2.107 3 g cm^{-3}, D_m = 2.103 1 g cm^{-3}. The structure was solved by Patterson method and successive Fourier syntheses gave location of all non-hydrogen atoms. The final R factor was 0.062 and R_w = 0.073 for 12869 reflections with $|F_o| > 5\sigma|(F_o)|$. The coordination polyhedron of Nd atoms comprises of seven oxygen atoms from the glycine and two from water molecules. There are two types of Nd–gly contacts. The presence of oxygen bridges explains considerable difference in the Nd–Nd distances. There was stated the difference in the neodymium–glycine bonding mode in comparison with that observed for calcium–glycine complex.

B21

Derivatives of Hydrogen Uranyl Phosphate: Excited-state Properties of a Family of Lamellar Solids

ARTHUR B. ELLIS*, MICHAEL M. OLKEN and RICHARD N. BIAGIONI

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wis. 53706, U.S.A.

The excited-state properties of the layered compound hydrogen uranyl phosphate (HUP), $HUO_2PO_4\cdot4H_2O$, and of solids derived therefrom by intercalative ion-exchange reactions have been examined. The reactions exploited are given in eqn. (1)–(3).

$$HUO_2PO_4 + M^+ \longrightarrow MUO_2PO_4 + H^+ \qquad (1)$$

$M = K, Ag, NH_4, NC_5H_6$ (pyridinium),

$n\text{-}C_4H_9NH_3, n\text{-}C_8H_{17}NH_3$

$$HUO_2PO_4 + \tfrac{1}{2}M^{2+} \longrightarrow M_{1/2}UO_2PO_4 + H^+ \qquad (2)$$

M = Ca, Zn, Cu (~0.4 equivalents incorporated)

$$HUO_2PO_4 + 1/3\ M^{3+} \longrightarrow M_{1/3}UO_2PO_4 + H^+ \qquad (3)$$

M = $Cr(urea)_6$, Eu (~0.07 equivalents incorporated)

The products of these reactions have all been characterized by elemental analysis, IR spectroscopy, and X-ray powder diffraction. The latter reveals that all of the compounds retain the lamellar structure of HUP and can be indexed in tetragonal symmetry, using c lattice values derived from 001 data and a lattice values of ~6.99 Å. Although the a values are roughly constant, the interlamellar spacings (distance from the middle of one layer to the middle of the adjacent layer) vary widely; typical values are 8.69, 9.01, 10.34 and 18.76 Å for HUP, NH_4UP, $Ca_{1/2}UP$, and $n\text{-}C_8H_{17}NH_3UP$, respectively.

All of the samples exhibit electronic absorption spectra characteristic of the UO_2^{2+} chromophore; for substituent cations possessing visible absorption bands, these transitions appear superimposed in each spectrum. Except for the $n\text{-}C_8H_{17}NH_3^+$, Ag^+, Cu^{2+}, and $Cr(urea)_6^{3+}$ salts, the samples all exhibit yellow-green emission characteristic of the UO_2^{2+} moiety when excited with blue or near-UV light at 295 K. Emission decay curves are exponential for all of the emissive solids and yield lifetimes, τ, ranging from ~1–450 μs. Samples having τ values of ~10^2–10^3 μs include HUP and the NH_4^+, pyridinium$^+$, K^+, Ca^{2+}, and Zn^{2+} derivatives. These solids also have radiative quantum efficiencies, ϕ_r, approaching unity at 295 K. Values of τ and ϕ_r have been used to calculate