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

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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 $Nd(gly)_3(ClO_4)_3 4\cdot 5H_2O$ 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

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The excited-state properties of the layered compound hydrogen uranyl phosphate (HUP), $HUO_2PO_4\cdot 4H_2O$, 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-$C_4H_9NH_3$, n-$C_8H_{17}NH_3$

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

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-$C_8H_{17}NH_3UP$, 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-$C_8H_{17}NH_3^+$, 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 radiative (k_r) and nonradiative (k_{nr}) are constants for excited-state decay. Values of k_r are nearly constant at ~(1–2) × 10^3 s^{-1} for the samples, whereas k_{nr} values span several orders of magnitude.

Possible quenching mechanisms for the weakly emissive and nonemissive samples include excited-state energy transfer (Cu^{2+}, Eu^{3+}, and $Cr(urea)_6^{3+}$ derivatives), electron transfer (Ag^+ and Cu^{2+} derivatives) and H-atom abstraction ($n\text{-}C_4H_9NH_3^+$ and $n\text{-}C_8H_{17}NH_3^+$ derivatives). Partially Eu-substituted HUP provides evidence for excited-state energy transfer: both the UO_2^{2+}-based emission and pink Eu^{3+} luminescence are simultaneously observed upon excitation of of the UO_2^{2+} chromophore. The relative intensities of the two types of emission vary with the Eu content in both this system and Eu-substituted $Ca_{1/2}UP$ samples. Concentration effects on luminescence have also been investigated with Ag-substituted KUP. The UO_2^{2+}-based emission is partially quenched in samples prepared from solutions in which the Ag:K ratio is as little as ~1:10,000. Some evidence for an exciton mechanism has been obtained in these studies.

Derivatives of HUP based on cationic transition metal complexes such as $Cr(urea)_6^{3+}$ afford interesting comparisons of excited-state properties with solution environments. To illustrate, the Cr complex exhibits fluorescence and phosphorescence at 77 K in an EPA glass. Absorption bands due to this complex are relatively unaffected when the complex is incorporated into the HUP lattice (λ_{max} ~ 625 nm), but no emission is observed from the solid at 77 K. These observations illustrate the role of environment on excited-state processes and the versatility of HUP as a host lattice for evaluating environmental effects.

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The Electronic Structures of Adducts of Lanthanide-(III) Tricyclopentadienides

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Adducts of the rare earth tricyclopentadienides ($Cp_3Pr{\cdot}add$) were first described by Birmingham and Wilkinson in 1954. Since then their chemistry and geometrical structures have been extensively studied. Although excellent optical spectra were reported by Pappalardo *et al.* at the end of the sixties, nothing is known about their electronic structures. The main reason for this is that they don't crystallize into single crystals which are suitable for optical measurements. Therefore they can only be studied in solution and the additional information obtained from polarized optical single crystal measurements is missing. In solution comparable information may be obtained by performing magnetic circular dichroism measurements.

By studying the cold and hot MCD transitions, 14 crystal field levels of $Cp_3Pr{\cdot}CNC_6H_{11}$ could be identified. After fitting this truncated crystal field splitting pattern, 36 bands in the low temperature absorption spectrum could be assigned. By fitting the energies of these 36 levels, a refined set of parameters was obtained. On the basis of this parameter set the low temperature absorption spectra of the adduct $Cp_3Nd{\cdot}MeTHF$ could also be explained.

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^{11}B NMR Studies on some Uranium(IV) Poly-(pyrazol-1-yl) Borate Complexes

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Although no full X-ray structural data are available yet for the actinide complexes of the poly-(pyrazol-1-yl)borates, a good deal of information has been obtained from their electronic and ^1H NMR spectra.

In this work results from ^{11}B NMR spectroscopy will be presented and a correlation with the above data is attempted. The compounds studied were of the type $UCl_x[H_nBL_{4-n}]_{4-x}$ where L = pyrazole or 3,5-dimethylpyrazole.

In spite of the broad lines observed in these compounds, the spectra are simple, and in some cases the large chemical shifts of some paramagnetic species seem to be quite helpful.

The spectra of the compounds $UCl_2[HB(3,5Me_2\text{-}Pz)_3]_2$ and $UCl_2[H_2B(3,5Me_2Pz)_2]_2$ in tetrahydrofuran display two lines, one with a small isotropic shift and another with a large isotropic shift. Titra-

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