

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 $\text{Ln}^{3+}$ 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  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Eu}^{3+}$  complexes with glycine, alanine and glutamic acid were synthesized and obtained in a form of monocrystals. Absorption and luminescence spectra recorded in the region of  $8000-35000\text{ cm}^{-1}$  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  $\text{Nd}(\text{gly})_3(\text{ClO}_4)_3 \cdot 4 \cdot 5\text{H}_2\text{O}$  is reported. Crystals are triclinic, space group  $P\bar{1}$ , with  $a = 11.554(4)\text{ \AA}$ ,  $b = 14.108(1)\text{ \AA}$ ,  $c = 15.660(3)\text{ \AA}$ ,  $\alpha = 97.11(1)^\circ$ ,  $\beta = 102.82(2)^\circ$ ,  $\gamma = 105.20(2)^\circ$ ,  $V = 2355.25\text{ \AA}^3$ ,  $Z = 4$ ,  $M.W. = 747.7$ ,  $D_c = 2.107\text{ g cm}^{-3}$ ,  $D_m = 2.103\text{ g cm}^{-3}$ . 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  $|F_o| > 5\sigma|F_c|$ . 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.

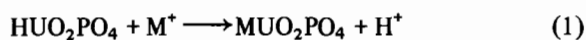
## B21

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

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

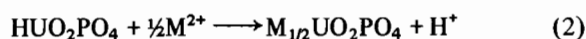
*Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wis. 53706, U.S.A.*

The excited-state properties of the layered compound hydrogen uranyl phosphate (HUP),  $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , and of solids derived therefrom by intercalative ion-exchange reactions have been examined. The reactions exploited are given in eqn. (1)–(3).

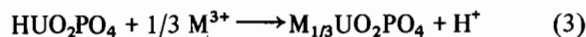


$\text{M} = \text{K}, \text{Ag}, \text{NH}_4, \text{NC}_5\text{H}_6$  (pyridinium),

$n\text{-C}_4\text{H}_9\text{NH}_3, n\text{-C}_8\text{H}_{17}\text{NH}_3$



$\text{M} = \text{Ca}, \text{Zn}, \text{Cu}$  ( $\sim 0.4$  equivalents incorporated)



$\text{M} = \text{Cr}(\text{urea})_6, \text{Eu}$  ( $\sim 0.07$  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  $\sim 6.99\text{ \AA}$ . 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  $\text{\AA}$  for HUP,  $\text{NH}_4\text{UP}$ ,  $\text{Ca}_{1/2}\text{UP}$ , and  $n\text{-C}_8\text{H}_{17}\text{NH}_3\text{UP}$ , respectively.

All of the samples exhibit electronic absorption spectra characteristic of the  $\text{UO}_2^{2+}$  chromophore; for substituent cations possessing visible absorption bands, these transitions appear superimposed in each spectrum. Except for the  $n\text{-C}_8\text{H}_{17}\text{NH}_3^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Cr}(\text{urea})_6^{3+}$  salts, the samples all exhibit yellow-green emission characteristic of the  $\text{UO}_2^{2+}$  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,  $\tau$ , ranging from  $\sim 1-450\text{ }\mu\text{s}$ . Samples having  $\tau$  values of  $\sim 10^2-10^3\text{ }\mu\text{s}$  include HUP and the  $\text{NH}_4^+$ , pyridinium $^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Zn}^{2+}$  derivatives. These solids also have radiative quantum efficiencies,  $\phi_r$ , approaching unity at 295 K. Values of  $\tau$  and  $\phi_r$  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  $\sim(1-2) \times 10^3 \text{ s}^{-1}$  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 ( $\text{Cu}^{2+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Cr}(\text{urea})_6^{3+}$  derivatives), electron transfer ( $\text{Ag}^+$  and  $\text{Cu}^{2+}$  derivatives) and H-atom abstraction ( $n\text{-C}_4\text{H}_9\text{NH}_3^+$  and  $n\text{-C}_8\text{H}_{17}\text{NH}_3^+$  derivatives). Partially Eu-substituted HUP provides evidence for excited-state energy transfer: both the  $\text{UO}_2^{2+}$ -based emission and pink  $\text{Eu}^{3+}$  luminescence are simultaneously observed upon excitation of the  $\text{UO}_2^{2+}$  chromophore. The relative intensities of the two types of emission vary with the Eu content in both this system and Eu-substituted  $\text{Ca}_{12}\text{UP}$  samples. Concentration effects on luminescence have also been investigated with Ag-substituted KUP. The  $\text{UO}_2^{2+}$ -based emission is partially quenched in samples prepared from solutions in which the Ag:K ratio is as little as  $\sim 1:10,000$ . Some evidence for an exciton mechanism has been obtained in these studies.

Derivatives of HUP based on cationic transition metal complexes such as  $\text{Cr}(\text{urea})_6^{3+}$  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 ( $\lambda_{\text{max}} \sim 625 \text{ nm}$ ), 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.

## B22

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

H.-D. AMBERGER\*<sup>†</sup> and N. M. EDELSTEIN

*Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, Calif. 94720, U.S.A.*

Adducts of the rare earth tricyclopentadienides ( $\text{Cp}_3\text{Pr}\cdot\text{add}$ ) 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

<sup>†</sup>Permanent address: Institut für Anorganische und Angewandte Chemie der Universität Hamburg, D-2000 Hamburg 13, Martin-Luther-King-Platz 6, F.R.G.

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  $\text{Cp}_3\text{Pr}\cdot\text{CNC}_6\text{H}_{11}$  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  $\text{Cp}_3\text{Nd}\cdot\text{MeTHF}$  could also be explained.

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## B23

### <sup>11</sup>B NMR Studies on some Uranium(IV) Poly-(pyrazol-1-yl) Borate Complexes

NOÉMIA MARQUES\*, A. PIRES DE MATOS

*Department of Chemistry, Institute of Energy, LNETI 2865, Sacavém, Portugal*

and K. W. BAGNALL

*Department of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.*

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 <sup>1</sup>H NMR spectra.

In this work results from <sup>11</sup>B NMR spectroscopy will be presented and a correlation with the above data is attempted. The compounds studied were of the type  $\text{UCl}_x[\text{H}_n\text{BL}_{4-n}]_{4-x}$  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  $\text{UCl}_2[\text{HB}(3,5\text{Me}_2\text{Pz})_3]_2$  and  $\text{UCl}_2[\text{H}_2\text{B}(3,5\text{Me}_2\text{Pz})_2]_2$  in tetrahydrofuran display two lines, one with a small isotropic shift and another with a large isotropic shift. Titra-