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## LOW DIMENSIONAL MAGNETIC SOLIDS AND SINGLE CRYSTAL ELPASOLITES:

## NEED FOR IMPROVED CRYSTAL GROWING TECHNIQUES

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and

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A series of  $\alpha$ -amido acid complexes of first row transition metals have been prepared which crystallize as infinite linear chains and exhibit low dimensional magnetic ordering (one or two) at temperatures below 40°K. The synthetic method appears quite general and a variety of materials can be systematically prepared. Correlations of molecular structure and magnetic properties should provide access to design protocols for developing materials with specific properties and sufficient experimental data to evaluate existing and proposed theoretical models for magnetic interactions between localized metal ion sites. To date, most experiments have produced only small crystals which have a tendency to be twinned or to contain imperfections. Crystals suitable for single crystal X-ray diffraction have been grown with difficulty. The need for extensive crystal growing experiments to develop techniques for preparing crystals suitable for magnetic anisotropy measurements and detailed X-ray and neutron diffraction studies is rationalized on the basis of the unique magnetic properties of the materials and their hydrogen bonded structures which have many features in common with metalloenzyme and metalloprotein active sites.

The rare earth complexes which crystallize in the cubic Elpasolite structure ( $\text{Cs}_2\text{NaLnCl}_6$  where Ln is a trivalent lanthanide) provide materials for carrying out detailed and relatively unambiguous investigations of the spectroscopic properties associated with f-f excitations or emissions localized on the lanthanide ions. This crystal system has begun to yield information concerning the energy transfer processes that take place when two different lanthanides are present and certain formulations appear to be possible candidates for microlasers. Single crystals of the single and mixed lanthanide species are prepared by the Bridgeman technique of gradient solidification of molten samples. The effects of crystal imperfections on the optical properties of these materials are an important part of the projected research to be done in this area. Extensive crystal growing studies on the  $\text{Cs}_2\text{NaLnCl}_6$  systems and the analogous  $\text{Cs}_2\text{NaLnF}_6$  systems can be justified in terms of the importance of the fundamental optical studies which are possible on single crystals of these materials and the possible relationship between crystal imperfections and luminescent properties and phase transitions.

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INTRODUCTION

At the present time, an interdisciplinary group from the Colleges of Chemistry and Physics and Engineering at Louisiana State University are developing an integrated research program in Material Science. One major component of this research is the synthesis and characterization of new inorganic materials which exhibit unique magnetic and optical properties. The ultimate potential of the research is limited by our ability to grow suitable single crystals and to definitely assess the effects of crystal imperfections. Crystal growth and solidification phenomena have been identified as fundamental areas to be investigated in the NASA program for materials processing in space and this Fluids Experiment System Workshop has included significant discussions on crystal growth experiments. Thus it appears that extensive crystal growth studies are priority activities for this program. The questions to be answered are: What materials will be chosen for study and what measurements and observations will be made? It would appear that the materials to be investigated should have the following characteristics: (1) they must have some intrinsic scientific or technological significance; (2) they must be complex enough that significant new information can be gained; and (3) they should be easily available and not prohibitively expensive since many ground-based experiments will be required. It would appear that two specific problems from the Material Science Group at LSU fit these requirements very well. One is the preparation of good quality single crystals of transition metal complexes with  $\alpha$ -amido acids from aqueous solution and the other is the preparation of single crystals of the highly symmetrical Elpasolites of the general formula,  $Cs_2NaLnX_6$  where Ln is a trivalent lanthanide and X is chloride

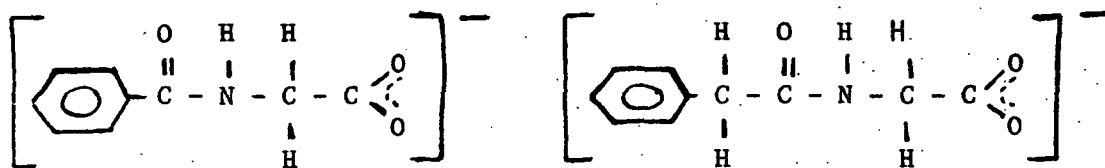
or fluoride. Both of these projects are presently underway [1] and extensive work on sample preparation has been done. However, little detailed research on the crystal growth process itself has been done and present funding does not include resources for such activity. The projects would exemplify two separate crystal growing problems. The low dimensional transition metal materials are prepared from aqueous and mixed aqueous-alcohol solutions of metal ion and ligand and are then recrystallized. The Elpasolites are prepared from high temperature melts of stoichiometric mixtures of the appropriate metal halides. Thus experiments devoted to single crystal growth in these projects should provide fundamental knowledge about the theory of crystal growth from aqueous solution and from high temperature melts. Outlined briefly below are the status of our research in these areas and the proposed ground work we feel needs to be done before space experiments are designed. The ability to provide extensive ground-based data on a variety of specific materials means that any projected space experiments would be clearly defined and adequate ground comparisons would be in place.

#### LOW DIMENSIONAL MAGNETIC MATERIALS

Chemists have routinely examined the magnetic properties of inorganic complexes at high temperatures ( $77^{\circ}\text{K}$  and above) where normal Curie or Curie-Weiss behavior is generally observed. For paramagnetic materials, the assumption has usually been made that they are magnetically dilute and the calculated susceptibility data have been used to determine the magnetic moment of the metal ion and the presence of low symmetry, and to deduce the Boltzmann distribution between the ground electronic state and thermally accessible excited states. Current cryogenic

technology has now progressed to a point where many materials are characterized at very low temperatures,  $4.2^{\circ}\text{K}$  and below. At these temperatures, deviations from Curie and Curie-Weiss behavior are common and new information about cooperative magnetic phenomena can be correlated with molecular and atomic structure. Mathematical models for such interactions have been a long-time interest of theoretical physicists and the determination of structural and magnetic data for a variety of magnetically non-dilute systems provides the necessary focus for the refinement and ultimate utility of such models [2]. We have now prepared and characterized one such set of compounds, a series of first row transition metal complexes of  $\alpha$ -amido acids which crystallize as linear chains and exhibit low-dimensional magnetic properties.

Earlier communications [3,4,5] from our laboratory have reported the structure and magnetic properties for the essentially isostructural cobalt (II), nickel (II) and iron (II) hippurates (hippurate is  $\text{C}_6\text{H}_5\text{CONHCH}_2\text{CO}_2^-$ ; see Figure 1) which have been characterized as canted, linear chain systems and have molecular formulas of  $\text{M}(\text{hipp})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ . The site symmetry of the metal ions was essentially  $\text{C}_{2h}$  (see Figure 2) with two hippurate ions (bonded through a single carboxyl oxygen) and two water molecules in the central plane and two bridging (through the oxygen atom) water molecules in the axial positions. The unit cell (see Figure 3) indicated that the linear chains were arranged in "rows" with interchain hydrogen bonding (see Figure 4 and 5) [6]. The intrachain metal-metal distance was about  $4\text{\AA}$  and the interchain distances were approximately  $7\text{\AA}$  within the "rows" and  $20\text{\AA}$  between "rows". In the Co(II) and Ni(II) cases, antiferromagnetic superexchange was postulated to occur along the chains (c axis) via bridging water molecules.



hippurate anion

phenaceturate anion

Figure 1: Structures of  $\alpha$ -Amido Acid Ligands

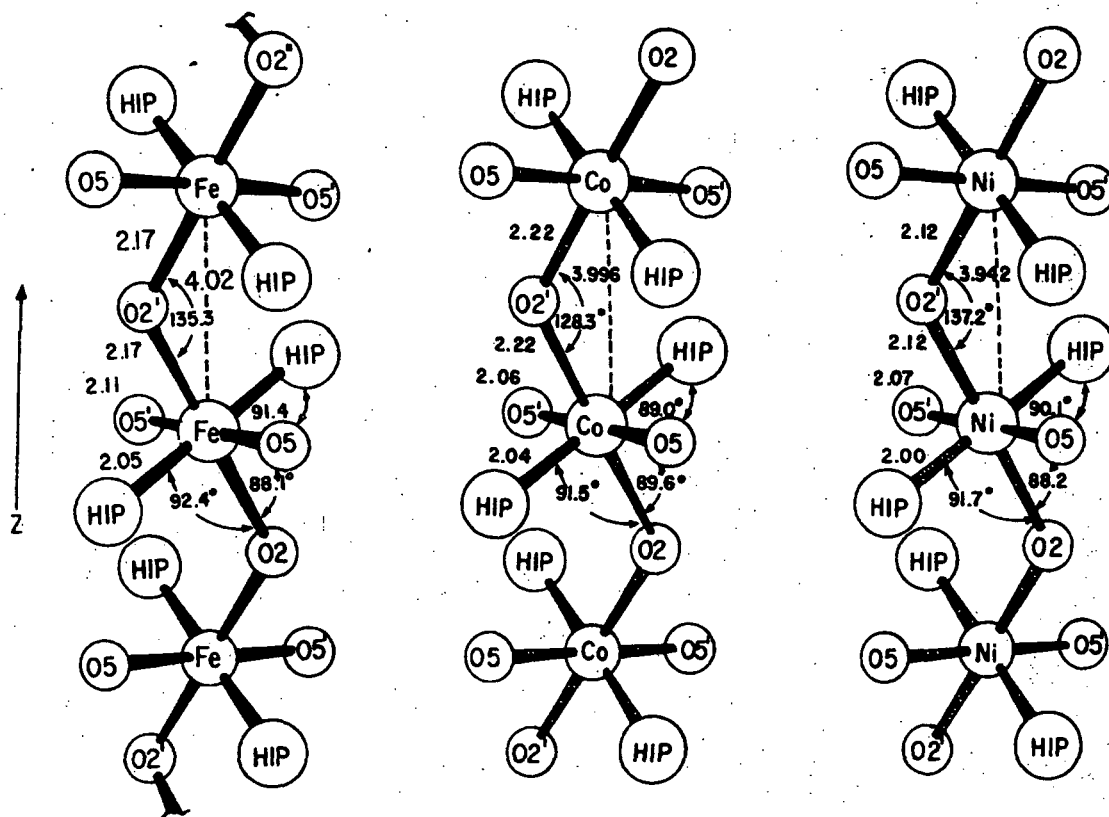


Figure 2: Projection View of the Site Symmetry About the Fe(II), Co(II) and Ni(II) ions in the Hippurate Complexes.

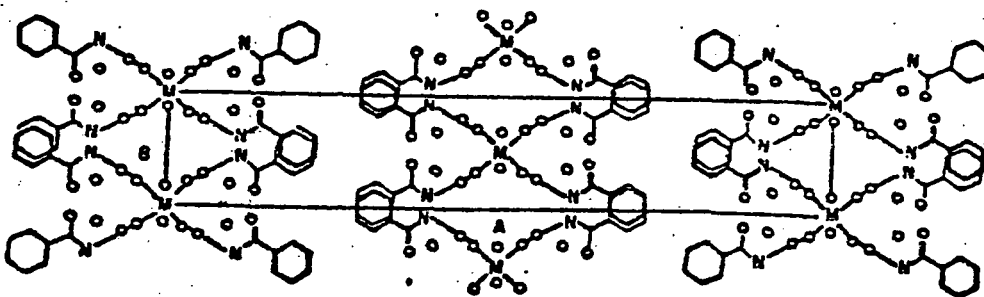


Figure 3: The Unit Cell of the Fe(II), Co(II), and Ni(II) Hippurates as Viewed Down the c Axis lines.

Since alternate spins were canted with respect to one another along the chains, the spin anisotropy of the Ni(II) and Co(II) ions was expected to generate a net spontaneous moment along the chain through the D-M (Dzyaloshinsky-Moriya) interaction [7,8,9]. In addition to this magnetic order along the chains, a low temperature transition was attributed to dipole-dipole interactions between neighboring chains in the "rows" (along the short or b axis) which resulted in the antiferromagnetic coupling of adjacent chains. The stylized model of this two-dimensional system is shown in Figure 6.

The corresponding Fe(II) hippurate was examined by Mössbauer spectra at low temperatures as indicated in Figure 8. A summary of the proposed description of the magnetic and electronic properties of  $\text{Fe(hipp)}_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  are as follows: (1) Single ion magnetic moments lie essentially in the x-y plane defined by the coordinate system of the electric field gradient, i.e.  $^5\text{B}_{2g}(\text{d}_{xy})$  electronic ground state; (2) Isotropic superexchange aligns the spins antiparallel along the chain or c axis; (3) Anisotropic superexchange occurs along the chain and results

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in a weak net spontaneous (D-M) moment directed parallel to the crystallographic a cell axis; (4) A sharp saturation in the superexchange ordering below  $T_c$  indicates the Ising behavior of the Fe(II) ion; and (5) Interchain interactions are not predicted to occur until  $T \rightarrow 0^\circ\text{K}$ . Thus we conclude that the Fe(II) hippurate is a unique example of a one-dimensional Ising chain system.

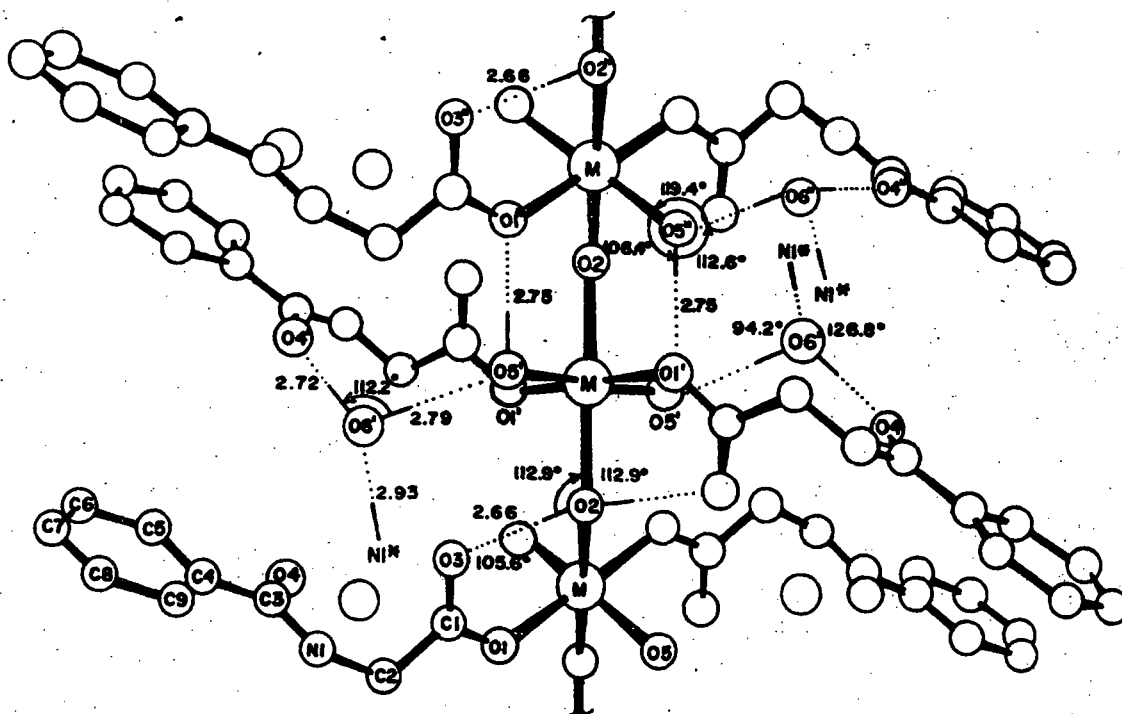


Figure 4: The  $M(\text{hip})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  Molecule. (Hydrogen bonding interactions are shown as dashed lines, while the solid portion of each dashed line represents the position of the hydrogen atoms.)

Figure 5: Proposed Interchain  
Hydrogen Bonding Along  
the b Axis for the  
 $M(\text{hipp})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ .

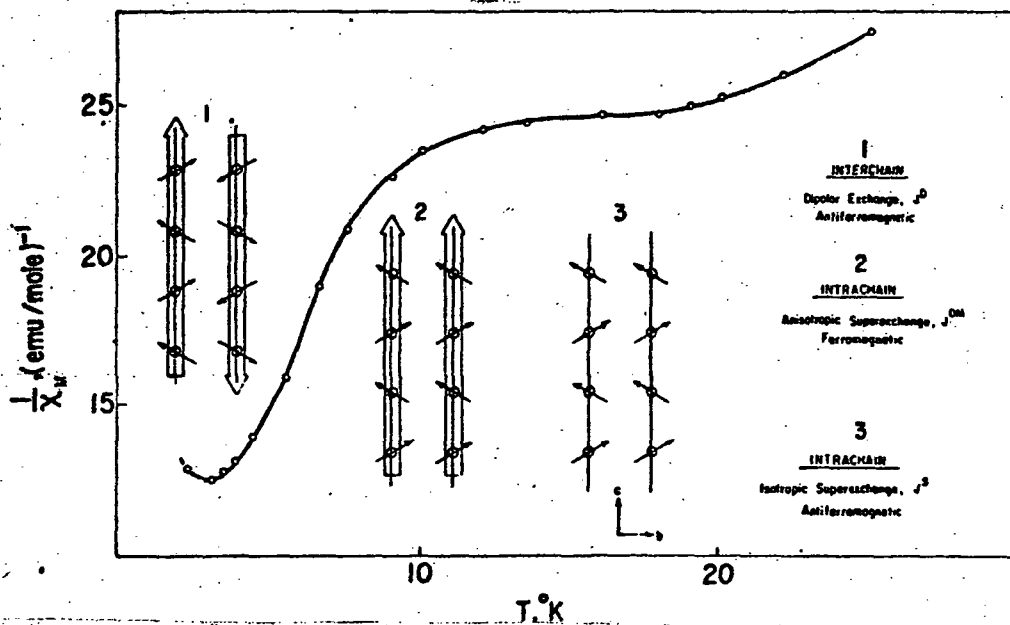
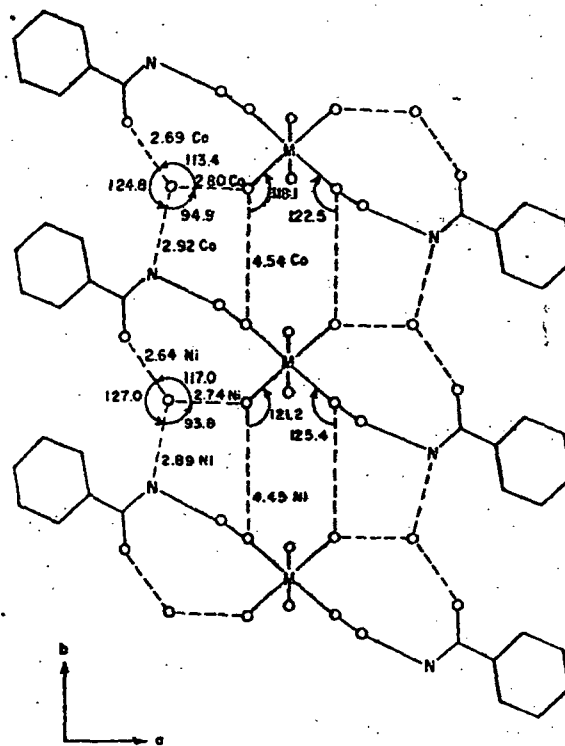


Figure 6: The Proposed Magnetic Spin Structure for the Ni(II) and  
Co(II) Hippurates (data points are for the Co(II) Complex).



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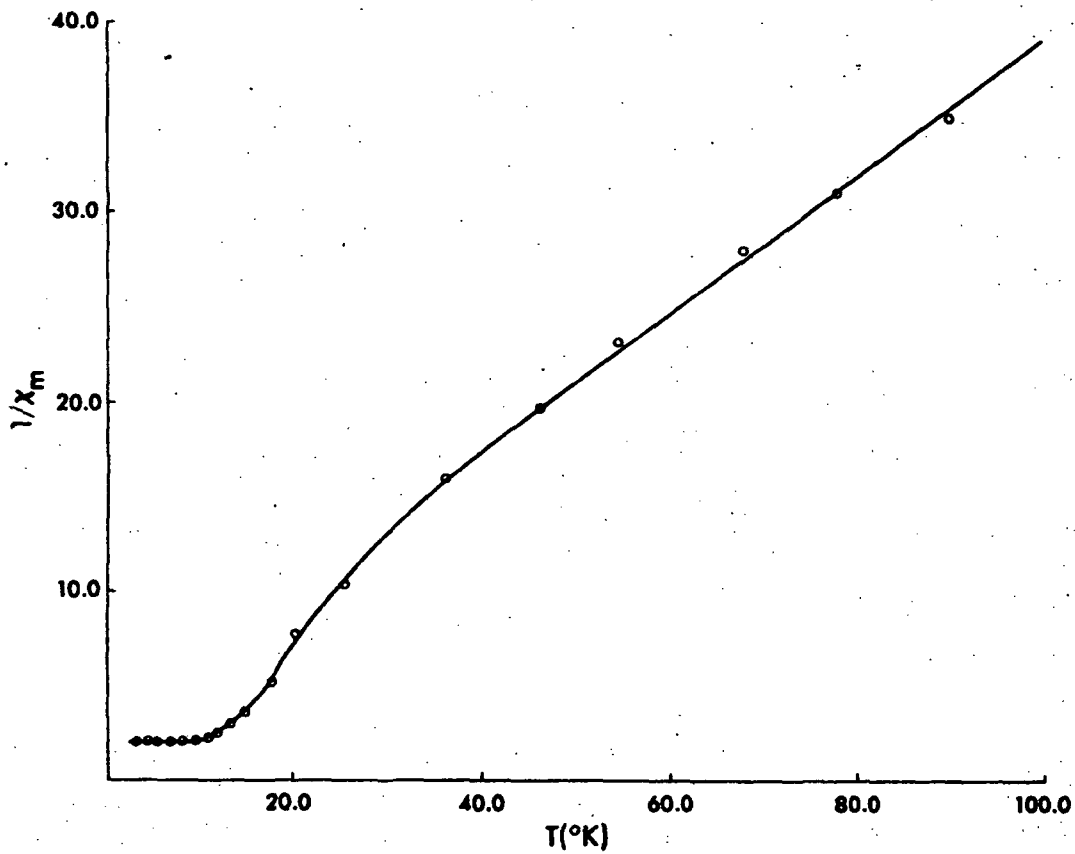
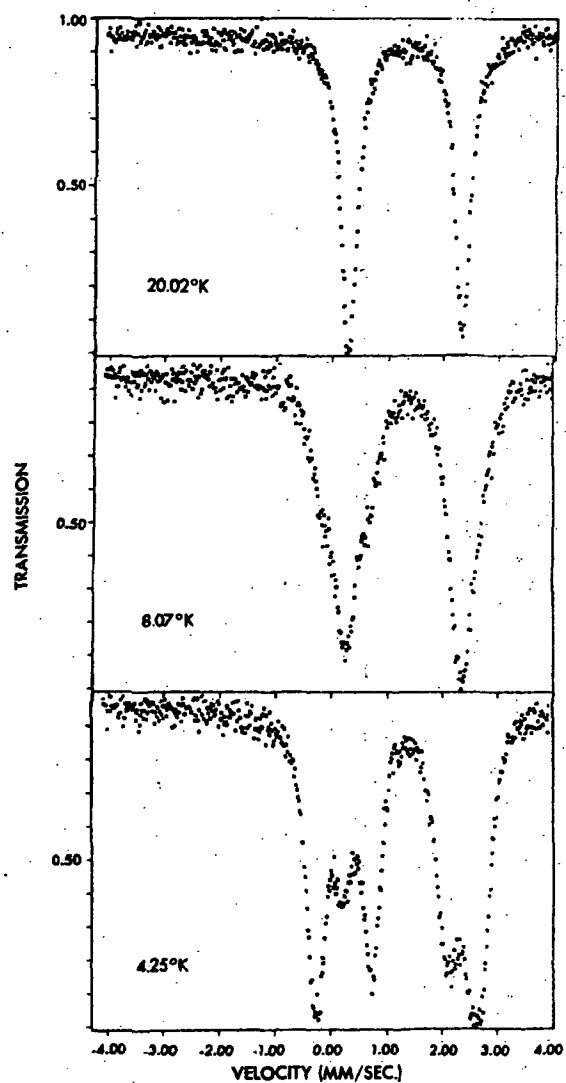


Figure 7: Inverse of the Magnetic Susceptibility vs. Temperature  
for a Powdered Sample of  $\text{Fe}(\text{hipp})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ .

Figure 8: Mössbauer Spectra of  
 $\text{Fe}(\text{hipp})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$



MÖSSBAUER SPECTRA OF  $\text{Fe}(\text{hipp})_2(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$

In addition to the Co(II), Ni(II) and Fe(II) hippurates, other similar ligands are being used to prepare new materials and other transition metal ions, notably Mn(II), are being investigated. These studies have provided new molecular systems for the evaluation of existing theoretical models and the extension of the work should provide an understanding of the relationship between structure and magnetic

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properties. Such understanding could ultimately lead to the strategic synthesis of new magnetic systems for practical applications.

ELPASOLITES: LANTHANIDE ION OPTICAL  
SPECTROSCOPY IN SYSTEMS OF HIGH SYMMETRY

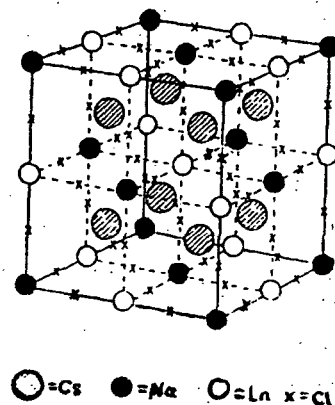
The preparation of materials that are efficient and useful phosphors, lasers, energy transfer or energy up-conversion systems is, to a large extent, still an empirical process. It is not yet possible to predict whether a material will have any of the above mentioned properties; nor is it practical to attempt any large scale design of materials with any of those properties. In certain cases some of the necessary properties are known (for example: in lasers two useful properties are high emission cross-sections and long radiative lifetime) but this is not true in general. The problem is exacerbated by the fact that even when it is known that certain properties are needed it is not always possible to choose in advance materials that have these desired properties.

All of the properties mentioned above are determined by the electronic states of the material and the interactions of these states with structural features. Thus if we are to be able to design materials for any of the above mentioned purposes, it is of prime importance to correlate the electronic structure and its interactions with the properties of interest. This requires materials which have the desired properties and can be studied in detail. The Elpasolite system,  $\text{Cs}_2\text{NaLnCl}_6$  (see Figure 9), with its isomorphs and its extensions, represents such a set of materials.

The bulk of work done to date on trivalent rare earth ions in the solid

state, has utilized crystal systems where the site symmetry of the rare earth ion was low enough to remove all but Kramer's degeneracy. This low symmetry leads to a great deal of crystal field and J-level mixing which makes it essentially meaningless to attach a specific label to a particular state and makes it difficult to obtain accurate metal wavefunctions [10,11]. In addition, in just about all cases which have been studied to date, no account has been taken of the mechanism by which the various transitions acquire intensity. Thus although the past work on rare earth spectroscopy has been voluminous, these two major weaknesses remain. No complete study has been made of trivalent rare earth ions at sites of known, precise, octahedral (6-coordinate) symmetry in the solid state where detailed assignments of existing states can be made and no thorough study of the intensity mechanisms for rare earth f-f transitions has been performed for a large number of these ions with identical, well defined crystal site symmetries. The work underway in Dr. Schwartz's laboratory on the Elpasolites is designed to rectify both of these situations [12-20].

Figure 9: One Unit Cell of  
 $\text{Cs}_2\text{NaLnCl}_6$



The luminescence properties of trivalent lanthanide ions at sites of  $O_h$  symmetry in the cubic crystal system  $Cs_2NaLnCl_6$  ( $Ln = Y^{3+}$  or trivalent lanthanide) are remarkable. Preliminary results indicate that in single crystals of  $Cs_2NaEuCl_6$  doped with  $Tb^{3+}$ , extremely efficient, long-range, energy transfer from  $Tb^{3+}$  to  $Eu^{3+}$  occurs.  $Cs_2NaHoCl_6$  has been observed to be a brilliant red emitter with an extremely high efficiency and  $Nd^{3+}$  in  $Cs_2NaNdCl_6$  and in  $Nd^{3+}: Cs_2NaYCl_6$  shows the longest lifetime of any  $Nd^{3+}$  compound. These three observations indicate that either alone, or in various combinations, lanthanide ions in crystals of this type could prove valuable in such diverse fields as commercial phosphors, laser materials, energy transfer or energy up-conversion systems.

#### CRYSTAL GROWING EXPERIMENTS

As the discussion above indicates, the thrust of our studies is to prepare new materials of high solid state quality (the linear chain magnetic materials) or to prepare well-defined and high quality crystals of rare earth ions in high symmetry environments. In other words we need high quality crystalline materials to study fundamentally important magnetic and optical phenomena. The two projects involve totally different crystal growing techniques. The magnetic materials are grown by mixing solutions of the metal ion and ligands and then recrystallizing from aqueous or mixed aqueous-achohol solutions. The rare earth Elpasolites are grown from the melts of stoichometric mixtures of the metal halides. Inorganic chemists in general have been interested in the properties of the materials synthesized and have had only peripheral interest in the detailed theory and mechanisms of material formation. Their approach to the improvement in crystal quality of their

preparations has been essentially empirical, i.e. try a proposed technique and harvest the resulting crystals. Thus the preparation of high quality crystalline materials has been an art form with success dictated by experience and luck. The two problems outlined here are no different. Recrystallization "recipes" have been used to prepare the small and imperfect linear chain crystals required for X-ray diffraction analysis and known temperature-gradient furnace techniques have been used to prepare the Elpasolites. In both cases, success has depended upon trial and error and experience. No basic information about crystal formation or crystal growing theory has been gained. However both problems rely heavily on the availability of high quality crystals and the low dimensional magnetic material studies have suffered because of the lack of crystals of sufficient size and quality to do single crystal magnetic measurements, heat capacity measurements, precise X-ray diffraction maps where hydrogen atoms can be located, and neutron diffraction experiments where hydrogen atoms can be found and spin structures determined. Thus the motivation for carrying out detailed crystal growing experiments is very high and the results, if successful, will provide materials of scientific and technological significance.

The possibility of carrying out crystal growing experiments in microgravity environments has re-kindled interest in the theory of crystal growing and the delineation of factors involved in single crystal growth. Carruthers [21, 22] has outlined the advantages of low gravity crystal growth and has delineated several ground-based problems which must be solved before full advantage can be taken of space development of new techniques and materials. Areas of concern include characterization and property measurements on materials of significant

technological interest and the definition of processes involved in crystal growth. Older theoretical approaches to crystal growth emphasize the lack of definitive experiments which test theories currently in vogue, particularly in the area of growth from solution [23, 24]. Thus it would appear that extensive crystal growing experiments on the materials of interest in this report would be timely and have high potential for future experiments designed specifically for low-gravity space environments. In both cases the starting materials are readily available and relatively inexpensive. Facilities required are fairly simple and for the most part, they already exist at LSU. A brief overview of the proposed experiments follow.

The linear chain, transition metal complexes of  $\alpha$ -amido acids have fairly complex, hydrogen bonded structures and it is not surprising that material recrystallized under ordinary conditions, with only cursory attention paid to control of growth variables, consisted of badly twinned or extremely small crystals. However, the fact that a more elaborate, re-crystallization growth procedure produced better crystals (although of minimal quality) would lead one to believe that high quality crystals are possible if the growth variables are understood and growth techniques are used which utilize that knowledge. Two approaches are possible: de novo synthesis, with crystallization controlled in part by chemical reaction kinetics and amounts of excess reagents; and controlled recrystallization of the pure compounds. Both approaches have been proposed and preliminary experiments carried out as a prelude to materials processing in space. Weiss and Lind [25, 26] have proposed techniques for growing crystals from the controlled mixing of two solutions containing the insoluble crystal components. Professor Authier

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of France has also designed a crystallization chamber for carrying out such experiments in space [27]. Lal [28] and Miyagarva [29] have designed experiments for recrystallizing large single crystals under controlled conditions, both with and without seed crystals. We would propose experiments of both types for our linear chain molecules. The gel method of Lind [25] has not been tried for materials of this type and should be investigated. Also variations of Professor Authier's crystallization vessel should be designed and controlled experiments carried out. However, it is anticipated that recrystallization techniques probably have the best chance of producing high quality crystals and our emphasis would be directed toward such studies. The first stage of activity would be to optimize the variables controlling spontaneous nucleation and growth from saturated aqueous solutions. Crystals obtained should be suitable for X-ray diffraction studies and for seeding growth of larger crystals in stage two experiments. These stage two efforts will be directed to the formation of large crystals by controlling precisely the degree of supersaturation and mass transport phenomena. Several different crystallization vessels have been proposed in the literature which could be used for initial design purposes [30, 31]. Crystal growth factors which will be investigated and optimized are: (1) the nature of the solvent; (2) the effects of additives and impurities upon morphology and material properties; and (3) the physical conditions of temperature, evaporation rate, and amount of agitation.

The current technique for preparing the Elpasolites is as follows. A stoichiometric mixture of the respective metal chlorides is evaporated to dryness and placed in a quartz tube having a tapered end (the tapered end facilitates the nucleation of the single crystal). The tube is



vacuum sealed and the single crystals are grown by the Bridgeman technique of gradient solidification of the molten sample. The furnace consists of a tube of alumina wound with nichrome heating wire. The winding of the heating wire is made nonuniform across the length of the tube so as to produce a temperature gradient along the length of the tube and to produce the highest temperatures at the center of the tube. The sample is lowered through the furnace by driving a slow moving motor which has a timer arrangement which can control the rate of travel of the sample. The time required to grow a good single crystal varies from a few days to several weeks. Similar techniques have been proposed (and some experiments carried out in Skylab) for crystal growth experiments from melts in low gravity environments [26, 32-34]. Of special interest is the preparation of single crystals of the fluoroelpasolite,  $A_2^I B^I M^{III} F_6$ . These materials are grown in a manner similar to that outlined above for the chlorospecies except that the fluoride starting materials are placed in a platinum or graphite crucible and melted down in a stream of dry  $N_2$  in a zone melting apparatus. This incongruently melting material is prepared in single crystal form by using a very slow travel rate through the furnace. Many single crystals of these materials will be prepared and their properties monitored by EPR, magnetic circular dichroism and optical spectroscopy. Special attention will be given to the effects of crystal imperfections in luminescent properties and crystalline phase transitions.

#### SUMMARY

We presently have programs of study underway where the ultimate success depends on our ability to prepare large, high quality single

crystals of transition metal and rare earth complexes. Extensive ground-based crystal growing experiments would provide definite data on optimization parameters which could be used to design significant crystal growing experiments in low gravity. The success of the program would be two-fold; new insight into the parameters which control crystal growth would be obtained; and new materials of intrinsic scientific and technological importance would be prepared and characterized.

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