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FUTURE DIRECTIONS IN SOLID STATE LANTHANIDE AND ACTINIDE CHEMISTRY

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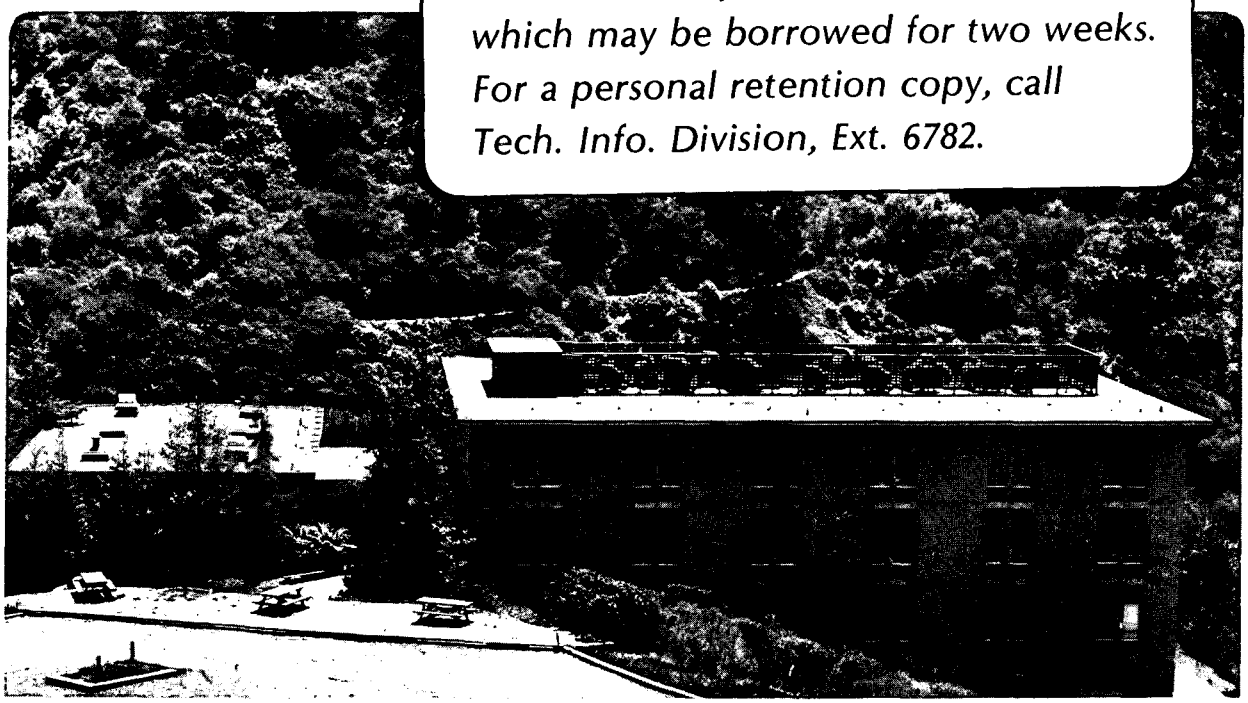

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FUTURE DIRECTIONS IN SOLID STATE LANTHANIDE AND ACTINIDE CHEMISTRY

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Summary

This paper reviews recent accomplishments and identifies current challenges in the syntheses and elucidation of bonding and electronic structure of metals, inorganic compounds, and organometallic compounds containing the rare-earth and actinide elements.

I. Introduction

It is possible to name several research subjects that barely existed a decade ago but are now topics of symposia or even of entire conferences: valence fluctuation, electron itinerancy, organo-f-element compounds, metal clusters, and incommensurate structures. In each of these areas the behavior of solids containing lanthanides and actinides is of central importance. Likewise, many new techniques of solid-state science (photoemission spectroscopy, SQUID susceptometry, laser spectroscopy, neutron scattering, Mössbauer spectroscopy) are powerful tools for investigating solids containing f-block elements. These new solid-state phenomena and new solid-state measurement methodologies have gone hand in hand in developing this field.

Periodic conferences and review articles have been devoted to solid-state f-element chemistry and physics; workshops and discussion groups have aimed at research needs and trends. Although the production of pure rare earth materials is mature, the availability of macroscopic amounts of heavier actinides (Am, Cm, Bk, Cf, and Es) has generated many studies, new insights, and speculation on periodic properties and research perspectives among f-block elements. The purpose of this review is to summarize the most recent developments in this field with emphasis on its opportunities and challenges (1).

II. Sample Preparation

Extensive and major laboratory programs of synthesis of pure samples of f-block solids have led to innumerable determinations of

properties of these substances at many research centers throughout the world. Production of rare-earth metals, alloys, and compounds of unprecedented purity have been pioneered by the Ames Laboratory at Iowa State University. Parallel levels of purity, and the remarkable growth of single crystals of actinide metals, oxides, halides, chalcogenides, and pnictides have been achieved at the European Institute for Transuranics at Karlsruhe. Limits of sample availability have restricted most of the Karlsruhe preparations to the elements thorium through plutonium. Multimilligram samples of americium through californium metals and compounds have been carried out at Oak Ridge National Laboratory; these substances are typically of the high purity normally found only on the multi-gram scale. Future prospects for solid sample preparation lie in ingenious methods for making large single crystals containing much of the world's supply of nuclides such as ^{248}Cm or ^{249}Cf, and of making highly-dilute samples containing short-lived nuclides such as ^{249}Bk ($t_{1/2}$ 329 days) and ^{254}Es ($t_{1/2}$ 276 days).

Metals

We may take the lanthanide and actinide meals (through Es) as a class of well-characterized materials. Recent papers (2-8) have shown that the lanthanides (except for Eu and Yb) are trivalent metals. The cohesive energies of the lanthanide metals decrease from La to Sm and from Gd to Tm because the ground-state free atoms are usually divalent ($f^{n+1}s^2$) while the metals are trivalent ($f^n ds^2$). When the

divalent-trivalent promotion energies ($f^{n+1}s^2$-$f^n ds^2$) are added to enthalpies of sublimation, a smooth trend in corrected sublimation enthalpies, ΔH_s^*, is observed (2,3). The divalent rare earth metals, Eu and Yb, cannot be included in this correlation because the divalent-trivalent energy difference in these metals is itself estimated from the correlation. The smooth variation in ΔH_s^* allows us to estimate the excess stability of actual (divalent) vs. hypothetical lanthanide-like (trivalent) Eu metal as 84 kJ/mol; the corresponding difference for Yb is 24 kJ/mol. Johansson and Rosengren (9) estimated 75 and 50 kJ/mol^{-1} for the excess stability of divalent Eu and Yb metals.

The corresponding behavior of the actinide metals is much more complex. The light actinides parallel d transition metals and only at americium does true lanthanide-like behavior begin. (Parallel behavior will be presented in subsequent sections on several compound types.) Among the interesting properties that have been observed in actinide metals are the superconductivity of Pa and Am (predicted by Johansson (4,10) and the phase transitions in Am at high pressure (11). These phase transitions reflect the shift from magnetic (localized) to bonding (delocalized) f electrons as pressure increases and as the Am internuclear distances decrease.

Although qualitative trends in the thermodynamics of actinide metals (their enthalpy of sublimation and of solution in dilute acid) indicate a tendency toward divalency that culminates in an observed ΔH(sublimation) for Es that is smaller than that for either Eu or Yb,

the crystal structures of Am through Cf at normal temperature and pressure are all characteristic of trivalent metals; only Es (and possibly one infrequently-observed allotrope of Cf (8,12) appears to be divalent as a metal. Since the short half lives of all isotopes of elements beyond Es preclude preparation of pure samples of their metals and compounds, we must rely on systematic extrapolation to predict the thermodynamic properties of these elements. David and coworkers (5) have conducted an extensive and innovative program of electrochemical tracer-level experiments from which they have deduced many thermodynamic properties of the heavy actinides.

The major systematic discrepancy in the thermodynamics of actinide metals is the behavior of americium. As the 5f analogue of europium, americium was expected to be divalent as a metal ($5f^7s^2$) and to have a readily accessible divalent state in solution and in compounds ($5f^7$). Although neither of these properties has been found for Am, it does have an enthalpy of vaporization (284 kJ/mol^{-1}) significantly less than that of Pu (342 kJ/mol^{-1}) or Cm(387 kJ/mol^{-1}) (13). It has repeatedly been noted (2,3,8) that ΔH_s^* (Am) is substantially too large (by ~ 80 kJ/mol^{-1} in comparison with neighboring actinides) despite three independent and consistent determinations of its enthalpy of vaporization. A recent identification of the energy level of $^8H_{3/2}$ (f^6ds^2) in the Am I spectrum (neutral Am vapor) at 10683 cm^{-1} (127.8 kJ/mol^{-1}) (14) differs significantly from earlier estimates and yields ΔH_s^* (Am) = 284 + 128 = 412 kJ/mol^{-1}, a value quite consistent with values for neighboring actinides.

A very useful function for correlation of thermodynamic properties of metals with gaseous atoms and condensed states is P(M) (2) which represents the transition from trivalent f^n M^{3+}(aq) to trivalent $f^n ds^2$ M(g). Nugent et al. (2) predicted that P(M) for the $5f^7$ actinide Cm should decrease more than that for the corresponding lanthanide Gd, but that P(M) for the heavy actinides should increase again because of inter-f-electron repulsion energy differences between the gaseous atoms and the metals. Based upon limited thermochemical and eletrochemical data on Bk^{3+} through No^{3+}, David et al. (3) boldly predicted that P(M) for the heavy actinides would continue to decrease.

Two recent revisions of data points that contribute to the P(M) function for actinides deserve mention. The revised energy level of f^6ds^2 Am I mentioned above corrects an anomalous P(Am) value. A new measurement of the enthalpy of solution of trivalent Cf metal ($\Delta H^o = -577 \pm 5$ kJ/mol^{-1}) (15) revises P(Cf) to be entirely consistent with lighter elements. These results exemplify how data from divergent areas of chemistry, physics, and materials science can illuminate periodic trends in f element solid state science.

To determine the enthalpy of formation of Es^{3+}(aq) or Es_2O_3 would be an enormous challenge. An ingenious experiment using surface or differential scanning calorimetry might achieve suitable sensitivity on the 10-100 microgram scale. Such a measurement might refine the estimate of $E^o(Es^{3+}/Es^o)$ made by Samhoun and David (5) on the basis of a polarographic Es^{3+}/Es^o potential and an

estimated amalgamation energy. Thermodynamic experimentation for elements heavier than Es will be limited to tracer-level concentrations, but even vapor pressure measurements may be possible if it can be shown that tracer level Yb in Sr metal obeys Raoult's law or Henry's law.

Hydrides

Ward (6) has emphasized the unique behavior of actinide hydrides. AcH_2 and ThH_2 are most similar to the f^0 elements La and Hf: neptunium and higher hydrides resemble the heavy lanthanides. Unusual properties are found for Th through Pu hydrides, showing that the 5f band drops from a high, unoccupied level (ThH_2) through a metallic region (UH_3) into possible semiconducting phases ($PuH_{2.65}$ above 100 K). Ward has pointed out the need for resistivity and bulk magnetic measurements on americium and curium hydrides. Preparation of EsH_2, expected to be a saline hydride like EuH_2, would be extremely difficult but interesting (1f).

Halides

A traditional emphasis of halide chemistry (especially of fluorides and chlorides) is the study of high metal oxidation states with strong oxidants. A new focus among transition-metal halides is the preparation of halide clusters with unusually low formal metal oxidation states. This section will focus on both of these extremes.

New unstable fluorides of the lanthanides and actinides have

recently been reported. The synthesis of PrF_4 and of double fluorides like Cs_3TmF_7 by use of the powerful low-temperature fluorinating agent KrF_2 (16) represented a significant achievement. Evidence for higher-valent actinide fluorides using novel techniques such as thermochromatography (PuF_5, EsF_4, and CmF_6 (17-19)) and infrared spectroscopy (AmF_6 (20)) have not been confirmed by independent measurements; specifically, EsF_4 should be (and perhaps has already been) sought for by KrF_2 fluorination. Efforts by chemical (21) and photochemical (22) means to prepare PuF_5 have failed to date. The existence of AmF_6 if it indeed can exist at low temperature, should be confirmed by low-temperature Raman and electronic spectroscopy <u>in situ</u>, in a UF_6 matrix, or by vapor transport and subsequent reduction.

Successful preparation of complex fluorides, under conditions that fail for binary fluordies, suggests the possibility of fluorine oxidation of americium or californium to the pentavalent state in such compounds as $CsMF_6$. Am(V) is known in oxides, oxyfluorides, and carbonates as well as in solution, but the preparation of a Cf(V) fluoride or oxyfluoride would be especially interesting since the only evidence for Cf(V) is as a possible aquo ion (23).

Thermodynamic data on the halides of the rare earths, of thorium, and of uranium are very well established. There are of course some gaps, such as the di-iodides of the rare earths and of thorium, some of which are metallic. Among halides of the transuranium elements relatively accessible to measurement, the higher fluorides of

neptunium and plutonium have such unusual stabilities and apparently nonsystematic behavior that their themodynamic properties need to be determined by precision reaction calorimetry (24).

Lower oxidation state chemistry of rare-earth element halides has developed rapidly since the discovery of $NdCl_2$ and $TmCl_2$. In addition to saline dihalides (for which there are actinide parallels AmX_2 and CfX_2) there are metallic dihalides (e.g. LnI_2), "vernier" nonstoichiometric halides (e.g. Sm_6Br_{13})(25), and metal-cluster subhalides (e.g. Gd_2Cl_3 and LaCl) (26). Most recently, complex dihalides have been synthesized (22); unlike lower binary halides that usually require the rare-earth metal itself as reductant, these compounds can sometimes be prepared with alkali metals as reductant: $Li + TmCl_3 = LiTmCl_3$ (27). No analogues are known for any of these classes of reduced halides among the actinides: phase-diagram studies of the $Pu-PuCl_3$ system shows no compound formation and minimal miscibility between the end members (28).

Recently, evidence for new divalent lanthanides and Pu(II) and heavier divalent actinides has been found in molten-salt co-crystallization studies with $EuCl_2$, $SmCl_2$, $NdCl_2$, or $PrCl_{2+x}$ as reductant in a melt containing LnOCl, $LnCl_3$, and $SrCl_2$ (29). The co-crystallization coefficients lead to reduction potential <u>differences</u> between the elements under study and the reductant. Since these differences are small, even for lanthanides like Ce and Tb that were hitherto unknown in the divalent state except in CaF_2, independent confirmation of divalency for Pu and Bk (that appear from these co-crystallization

studies to be more stable than Nd(II)) are needed. Spectrophotometric, magnetic, or photoelectron spectral identification of divalency in these elements might be more reliable than traditional methods like phase studies (DTA) or x-ray diffraction.

The early transition elements display behavior different from the actinides in their lower oxidation states. Some of the early (d^1-d^5) transition metals yield low-valent metal-metal bonded dimeric halo-ions: $Cs_3W_2Cl_9$ has face-sharing WCl_6 octahedra with short W-W distances, and $Mo_2Cl_8^{2-}$ is one of many binuclear clusters exhibiting the very strong quadrupole bond (30). Other early transition metals display cluster arrays such as in Sc_5Cl_8 and $NaMo_4O_6$ (31), Chevrel phases Mo_6X_8 (32), or polymeric arrays found in LaCl and ZrCl (33,34). It is not at all certain that reduced actinide halides will always behave like their lanthanide analogues; in fact, light actinides may indeed exhibit behavior paralleling the Ti-Zr-Hf or Mo-W families. Such behavior has not been found: for example, no solubility was found in the U-UCl_3 system (35) although there is some solubility of uranium in UBr_3 and UI_3. Similarly, compounds such as K_2UCl_5 (36), and K_2PuCl_5 (37) show no tendency toward metal-metal bonding. The synthesis of molecular, cluster, or chain "polymer" compounds with actinide metal-metal bonds remains a major challenge.

Cerium(IV) is the only tetravalent lanthanide that can exist in chloride coordination. In addition to cationic hexachlorocerate(IV) complexes, Ce(IV) complexes with neutral donor ligands are now

known (38). Structural and coordination studies showed that $CeCl_4$ and UCl_4 complexes are similar, and that the UCl_4 complexes are preparable in higher yields (more stable). These and parallel studies with $(R_3N(CH_2)_nNR_3)UCl_6$ (39) indicate that similar complex chlorides should be sought for Pu, Am, and Bk, three actinides which do not have stable simple tetrachlorides. Such An(IV) complexes should be useful for spectroscopic studies and also as reagents in organoactinide(IV) syntheses.

Oxides

The chemical and physical properties of binary lanthanide and actinide oxides are well understood. For many purposes, complex oxide systems are more interesting. Phase diagrams and crystallographic properties are well characterized both in simple and complex oxides. Thermodynamic and magnetic properties of complex oxides are now under intense investigation. Studies that focus on electronic structure are now capturing attention with modern spectroscopic techniques, as are studies of relationships between structure and electronic properties, or between structure and thermodynamic properties.

Some important classes of compounds are the lanmthanide dioxides CeO_2, PrO_2, and TbO_2, and the corresponding complex perovskite oxides $BaLnO_3$. These two classes of compounds have been probed extensively, with measurements still being refined, by elastic and inelastic neutron scattering, thermodynamics, magnetic susceptibility at low temperature, and photoelectron spectroscopy. Their high

symmetry (cubic or nearly octahedral) leads to straightforward crystal field and band structure calculations that emphasize a bonding model based on the participation of f electrons in covalent and overlap interactions. Parallel studies have been done or are in progress (13,40) for a few actinide systems, e.g. UO_2 and $BaUO_3$ as well as CmO_2 and $BaCmO_3$. In the latter case there is unexpected evidence of significant Cm(III) remaining in these tetravalent Cm oxides (41).

Among complex oxides of lanthanides and actinides with alkali metals and alkaline earth metals, the thermodynamic behavior of tetravalent lanthanide and actinide oxides, pentavalent actinide oxides, and hexavalent actinide oxides is dependent on ionic size, coordination, and acid-base properties of the component oxides. The extent of stabilization of U(VI) and Np(VI) has been quantitatively determined in several complex oxides. In favorable cases (e.g., cesium or barium actinide complex oxides) the stabilization of An(IV), An(V), and An(VI) ions in a complex oxide such as $BaUO_{3+x}$ is ca. 80, 200, and 350 kJ/mol greater than in the corresponding binary oxides such as UO_{2+x} (42).

The electronic structures of lanthanide(III) and (IV) oxides, and to a limited extent of corresponding actinide oxides, have been characterized by magnetic susceptibility, EPR, neutron scattering, and photoelectron spectroscopy (43). Because of the diversity of actinide oxidation states, isoelectronic ions may be studied in similar coordination, as was done by Kanellakopulos et al. (44) for several $5f^2$ complex oxides by electronic spectroscopy and magnetic

susceptibility. Electron transport properties should be studied for such oxides to determine if delocalized f electrons contribute to semiconductor or metallic behavior.

Lanthanide monoxides have recently captured attention since they can be prepared in bulk at high pressure and since they may be conductors, semiconductors, or insulators (45). Earlier reports of lanthanide and actinide monoxides apparently are impure surface phases, oxynitrides, or oxycarbides (46). High-pressure preparations of AmO and CfO, as well as preparations of complex actinide(II) oxides, are highly desirable.

Chalcogenides, Pnictides, and Carbides

Damien and de Novion (47) have identified important problems in the characterization of the electronic configuration in actinide solids, especially the distribution among the 7s, 6d, and 5f subshells, because the "outer" (7s, 6d) electronic component contributes to itinerant (delocalized) 5f hybridized behavior when actinide ions are relatively close to one another. These properties are exhibited dramatically in crystallographic, magnetic, and electronic-transport phenomena in lanthanide chalcogenides and pnictides (47). Kaldis and coworkers (48) and Johnson (7) have shown that thermodynamic properties of lanthanide sulfides give evidence for transitions between divalent (f^{n+1}, semiconducting, localized) and trivalent (f^n metallic, itinerant) behavior. Thus it is the comparable group of actinide compounds in which localized-itinerant

transitions ("valence fluctuation") must be sought.

Powder x-ray diffraction studies have been carried out for chalcogenides (S, Se, and Te) and pnictides (N, P, As, and Sb) of actinides through Bk or Cf. For 1:1 NaCl-type compounds, the lattice constants show dramatically the change from tetravalent (UN, USe, etc.) to trivalent (AmN, AmSe) behavior. Susceptibility and electrical-conductivity measurements have been limited primarily to Chevrel phases such as $Np_{1+x}Mo_6Se_8$ (47) and oxide chalcogenides such as Pu_2O_2S (49), to locate superexchange coupling between actinide atoms with localized 5f electrons (antiferromagnetism) and superconductivity. Chevrel phases with actinide clusters such as U_6X_8 instead of Mo_6X_8 would be significant (32).

Organometallic Complexes of the Lanthanides and Actinides (50)

One of the most active areas of investigation in the last decade has been in the area of organometallic complexes of the lanthanides and actinides. The large ionic size of the f block ions compared to the d transition elements allows higher coordination numbers. In addition, the availability of f orbitals could result in different types of bonding than for the d transition elements because of differing symmetry properties of the metal ion orbitals. The degree of the participation of f orbitals in bonding is difficult to ascertain experimentally, and continues to be an active area of investigation.

Although Reynolds and Wilkinson first isolated the organometallic

complex Cp_3UCl in 1956 (51) ($Cp = C_5H_5^-$, the uranium ion is equidistant from each of the five carbon atoms in the cyclopentadienyl ring; this type of bonding is called pentahapto), the interest in organo f element chemistry was stirred by the synthesis of the sandwich compound uranocene, $U(C_8H_8)_2$, an f electron compound whose existence and stability was predicted from bonding analogies to ferrocene by Müller-Westerhoff and Streitwieser in 1968 (52). Since that time Streitwieser and his collaborators have extensively studied the chemical, physical and bonding properties of $M(C_8H_8)_2$ and analogous compounds, where M = Th, Pa, U, Np, Pu (53).

Another system which has excited great interest comprises the products derived from the compound bis(pentamethylcyclopentadienyl) MCl_2 or $[C_5(CH_3)_5]MCl_2$, $M = U^{4+}$, Th^{4+} where the substituted cyclopentadienyl rings are again pentahapto bonded to the metal ion (54). This work has recently been extended to Np^{4+} (55). (All $(R_5C_5)^-$, $R = H, CH_3$, ligands bonded to metal ions referred to in this paper have this type of bonding.) The steric bulk of the $[C_5(CH_3)_5]^-$ ligands blocks a number of coordination sites of the tetrapositive actinide ion, yet two ligands are still available for reactions. In addition, the methyl groups provide solubility of reagents and enhance the crystallization of the products of various reactions. Paralleling similar systems in the early transition metals (i.e., Ti, Zr), Marks and his coworkers (54) have extensively developed the rich chemistry of these systems. The types of molecules they have characterized include alkyls, hydrides, alkoxides, and

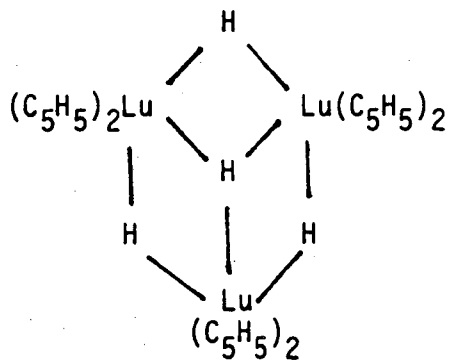
amides. They have also studied the activation of CO by a number of these systems. Recently, thermochemical measurements of Th-R bond strengths have been presented for some $[(CH_3)_5C_5]_2ThR_2$ compounds which highlight some of the differences in reactivity patterns between these compounds and the d transition metals (56).

In a related area of actinide chemistry, Andersen and coworkers have prepared and characterized phosphine complexes of Th^{4+} and U^{4+} (57). Previous workers had attempted to prepare such compounds but were either unsuccessful or their materials were not convincingly characterized. The importance of this work is that phosphines had been considered "soft" donors which would not bond with metal ions which are considered "hard". For example, it was thought that Th^{4+} or U^{4+} (hard metal ions) would bond only with ligands such as halides, amines, or ethers. In fact recent NMR solution measurements have shown that in complexes of the $(CH_3Cp)_3U$ L, where L = THF, tertiary amine, or PMe_3, (Me = CH_3), the PMe_3 ligand will replace both the ether and the amine (58). In a related area of coordination chemistry, Pinkerton and coworkers have investigated the bonding interactions between dithiophosphinate (S_2P-R_2) ligands (the bonding is through the "soft" donor S atoms) and the trivalent lanthanides and Th^{4+} (59).

Triscyclopentadienyl compounds of the trivalent lanthanides and actinides have been prepared and structurally characterized. The cyclopentadienyl and pentamethylcyclopentadienyl ligands have been utilized to prepare divalent lanthanide complexes of Yb, Eu, Sm, and

complexes of the type $[C(CH_3)_5]_2LnR$ and $(C_5H_5)_2LnR$ compounds where Ln = trivalent lanthanide ion and R = halide, alkyl, etc. (60). In an interesting application of electron-transfer reactions, Andersen and coworkers have utilized the divalent Yb complex as a reducing agent in a series of reactions with Fe or Co carbonyl compounds to form a series of $[C(CH_3)_5]_2Yb^{3+}$- Fe or Co carbonyl clusters where the Yb ion is bonded to the d transition metal carbonyl by bridging carbonyl groups (61). A related series of compounds of the type $Ln[Co(CO)_4]_2\cdot(THF)_n$ (THF = tetrahydrofuran; n = 3, 4; Ln = Sm^{2+}, Eu^{2+}, Yb^{2+}) were recently reported by Seleimanov and coworkers (62).

Evans and coworkers, and Watson, et al. (63,64) have been exploring the reaction chemistry of compounds of the type R_2LnR' (R = C_5H_5 or $C_5(CH_3)_5$, R' = Cl^-, CH_3, etc.) where the substitution for R' can be readily attained. One of the more unusual compounds prepared, $\{[C_5H_5)_2LuH]_3H\}\{Li(THF)_3\}$ has been reported by Evans, et al. (65). The anion has each of the three Lu atoms bridged by two H atoms as shown:



The purpose of this very brief introduction to organo-f element

chemistry is to give an indication of the present types of activities in the area. There is clearly much more work of this sort to do with the naturally occurring elements of the f transition series; however, almost no studies have been reported for any oxidation state of Pa or the transuranium elements except for the aforementioned triscyclopentadienyl An^{3+} compounds. The very rich organoactinide chemistry for U^{4+} and Th^{4+} should be further developed for Pa^{4+}, Np^{4+}, and Pu^{4+}. Some differences in the organoactinide chemistry of these elements can be anticipated because of their different oxidation-reduction potentials. Very few organometallic compounds of actinide oxidation states higher than tetrapositive have been prepared. For the transplutonium elements the primary accessible oxidation state is trivalent, and it might be anticipated that there would be only minor differences from trivalent lanthanide chemistry. These postulated similarities should be verified. In addition, the divalent state is accessible for Am, Cf, and Es, and a few tetravalent inorganic compounds have been characterized for Am and Bk. For the transcurium elements preparations on the milligram or smaller scale will need to be utilized. The goal of this type of research is to identify the similarities and differences between the f block and the d block transition series and to obtain unusual (and presently unknown) compounds containing, for example, metal-metal bonds between two lanthanide or actinide metals or between an f block and a d block element.

III. Characterization of Materials

Challenges of Research in the Actinide Series (66)

One of the most interesting properties of the actinide metals is that, as a function of atomic number, they undergo a transition around Am from essentially temperature-independent magnetism to localized temperature-dependent magnetism. This phenomenom can be explained by the early actinide metals exhibiting d-like (itinerant) behavior while the transplutonium elements exhibit 4f-like (localized) behavior. This crossover region occurs around Z = 94, 95 (Pu, Am), and consequently the crossover region and the elements before and after this region must be well-characterized experimentally in order to obtain a consistent description of this transition region. Effects intermediate between the d and 4f transition elements are found in the chemistry of the actinide elements and are the reason why the actinides were not accepted as a second f-transition series until the discovery and characterization of the transuranium elements.

In comparison with the d or 4f transition elements few studies have been reported for the transplutonium elements or their compounds. In order to characterize these materials, the wide variety of experimental techniques mentioned earlier (i.e. photo-emission spectroscopy, magnetic measurements, optical techniques, x-ray and neutron scattering, etc.) should continue to be utilized on all new materials.

Various transplutonium elements are available for experimental use in quantities 10-500 mg (^{243}Am, ^{248}Cm) down to 10-100 μg (^{253}Es). On the microscale impurity effects can dominate the

measurements. All materials must be carefully examined for purity and structure before measurements are reported; and different preparations of the same materials should be checked for reproducible results.

During the past decade, the quality of the general instrumentation available to study materials has increased enormously. For example, synchrotron radiation sources now allow use of variable wavelength ultra-violet or soft x-ray radiation for photoemission techniques. The use of high resolution lasers has revolutionized the practice of spectroscopy. As an example of the information which can be obtained by modern instrumentation, the information obtained from optical spectroscopy on insulating f electron compounds will be briefly discussed.

Application of Optical Techniques for the Study of Electronic Structure

Lanthanide and actinide insulating compounds are advantageous to study by optical spectroscopy because the spectra consist of many sharp lines at low temperature, which provide information about the electronic structure of the f shell. For both the 4f and 5f series, the trivalent ions have been extensively studied as impurities in single crystals of $LaCl_3$, and the systematics of the electrostatic, spin-orbit, and crystal field parameters have been evaluated as a function of atomic number (67). A number of other trivalent lanthanide ions have been examined in other systems (68).

The data available for other oxidation states of the lanthanide and especially the actinide series are rather meager. There have been

a number of studies of U^{4+} in various hosts, but the analyses are not as satisfactory as found for the trivalent ions. This may be because the strength of the crystal field is much larger in the tetravalent ions, so that inadequacies in the effective Hamiltonian presently used for analysis are becoming apparent (69). Clearly, the reasons for these discrepancies must be resolved.

With the advent of lasers, very high resolution data may now be obtained. In the future, data which are now obtained for ground states in crystals, such as hyperfine and vibronic structure, may also be measured in excited states (70). Studies on the energy splittings of an f^n configuration overlapping with a higher lying configuration in a crystal have already been reported (71). Time-dependent phenomena may readily be measured (72). The challenge in future years will be not only to explore f block ions in oxidation states and molecules which have not yet been addressed in a systematic way, but to return to what are considered to be well-understood materials and, with new techniques, to study phenomena which heretofore have been unattainable.

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