

Plenary and Session Lectures

D1

Recent Developments in the Chemistry of Element 96, Curium

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The preparation and properties of the following curium compounds will be reported: CmSi, Cm₂Si₃, CmSi₂, CmPO₄·xH₂O, Cm(ReO₄)₃·xH₂O, Cm(ReO₄)₃, Cm₂(WO₄)₃, CmVO₄, CmCrO₄, CmAsO₄, CmScO₃, CmVO₃, CmCrO₃, CmFeO₃, Cm₂(C₂O₄)₃·xH₂O, Cm(HCOO)₃. The special microchemical preparation techniques used in this work will be described in detail; lattice constants and other X-ray data will be reported.

D2

Lanthanide and Actinide Oxidation States in Complex Oxides and Halides*

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Complex oxides and halides of the lanthanides and actinides have been studied extensively and reviewed thoroughly. Trivalent lanthanides and tetravalent actinides are readily prepared as complex halides; these two classes of complex compounds have been thoroughly investigated. Among complex oxides the most important groups have been those of the trivalent lanthanides and the hexavalent actinides.

A number of recent research programs have been carried out on classes of complex compounds of unusual oxidation states. For example, exotic oxidation states such as Ln(II) and An(V) have been the focus of study of CsLnX₃ and MAnO₃ compounds (M = Li–Cs). In this category should also be placed the complex tetravalent oxides BaLnO₃ and BaAnO₃, since these compounds are relatively unstable (for different reasons).

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract number W-31-109-ENG-38.

This paper identifies some of the highlights of recent reviews cited above, and compares and contrasts the structural and thermodynamic properties of these important classes of compounds. 'Mixed oxides', such as LnLn'O₃ and An_xAn'_{1-x}O₂, are not treated here. Important predictions and areas for new research opportunities are identified.

D3

Crystal Field and Exchange Interactions in the Cubic Uranium Semimetallic Compounds

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(To be published later as a full paper)

D4

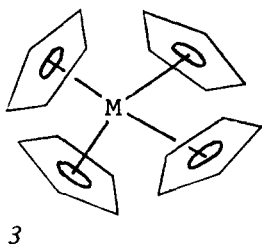
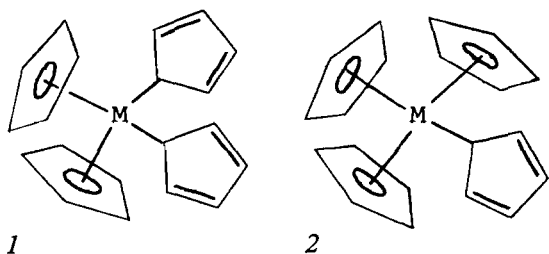
A Comparison of the Structural Parameters of Organolanthanide and -Actinide Complexes with those of Transition Metals in Similar Environments

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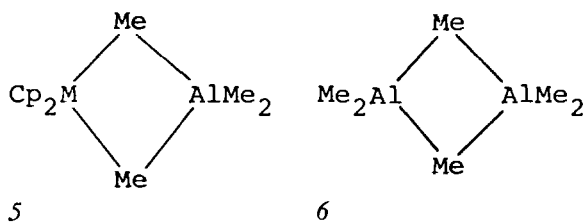
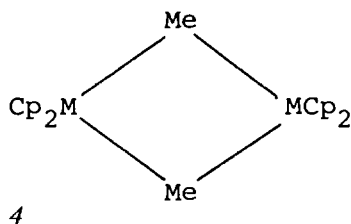
The organometallic chemistry of the lanthanides and actinides has undergone a vast expansion in the past few years. New types of structure and reactivity found today were unforeseen only a few years ago. A comparison of the chemistry of lanthanides and actinides to that of transition metals previously would have been rather insignificant, but now is of growing importance. This discussion will center on structural data and where possible its relevance to reactivity.

Our group interest in this topic arose from two different types of comparisons. First, the X-ray structural investigations of MCP₄ (M = Ti, Zr, Hf, U) provided interesting results. For M = Ti, 1 was found, while 2 pertained for M = Zr. Even though Hf and Zr differ by only 0.01 Å in ionic or metallic radii, M = Hf produced structural type 1, not 2. For the larger M = U, 3 was found by Burns. The 4+ ionic radii for



the four metals are 0.68, 0.74, 0.75, and 0.93 Å, respectively. Thus, the smaller Ti^{4+} opts for the formal coordination number of 8, and the larger U^{4+} takes a value of 12. Zr^{4+} and Hf^{4+} apparently sit in a delicate balance between these extremes.

A second source of initial interest was the comparison between $[Cp_2MMe]_2$ (4), $[Cp_2MMe_2-AlMe_2]$ (5) and $[Me_2AlMe_2-AlMe_2]$ (6). The structural similarities were such that the use of the term 'electron-deficient' to describe the bridge-bonding was irresistible.



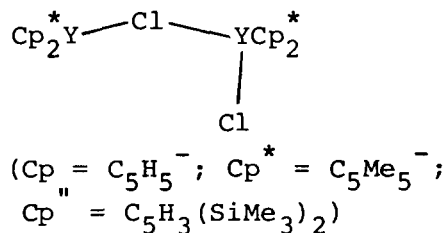
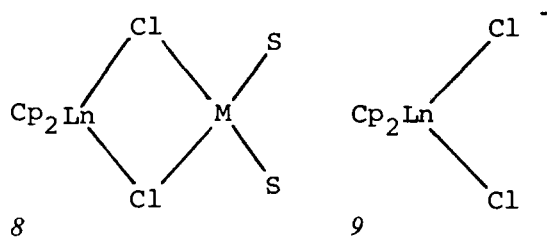
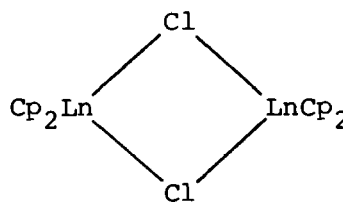
These studies appeared separately largely in the late 1970's. Now we are in a position to make a great many comparisons. The focus will be on ligand systems (L) in which $L = -Cl^-$, $-CR_3^-$, $-NR_2^-$, and $-OR^-$. Many studies have involved $-Cl^-$ and $-CR_3^-$, while relatively fewer are found for $-NR_2^-$ and $-OR^-$. However, some of the best comparisons are to be found $-OR^-$. We have dealt mainly with the early transition metals, and especially with Ti, Zr, and

Hf. These elements share a substantial oxophilicity with the lanthanides and actinides, and also both have a relatively uncomplicated redox chemistry.

In the paragraphs that follow emphasis will be placed on new structural data for three types of organolanthanides and -actinides. Finally, a mixture of new and exciting developments will be presented under the 'miscellaneous' heading.

Chloro compounds

As Lappert has pointed out, among the lanthanides there exist three major types of chloro derivatives, 7, 8, and 9 (where M = cations such as Li or Na and S = donor solvent). We have seen examples of

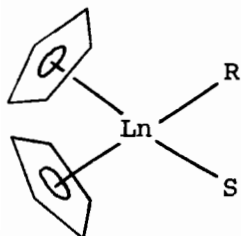


all three and have more recently uncovered yet a fourth species, 10. Here, the metal is specified as Y, although a similar structure probably is to be found for Yb, Lu, and other late-lanthanides. In the bridge the two Y-Cl lengths are 2.68 and 2.82 Å, and the terminal value is 2.74 Å. The Y-Cl-Y angle is 163° . The relevance of this structure to the chemistry of these elements will be discussed. We are seeking the point in the lanthanide series where the move from 7 to 10 occurs. The essential point is that the bulky Cp* ligands will not allow configuration 7 for the smaller (late) lanthanides.

Steric arguments can also be related to the structure and chemistry of Cp_2UCl_2 , $Cp_2''UCl_2$, and $Cp_2^*UCl_2$.

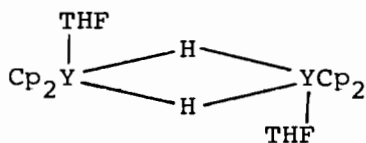
Alkyl, hydride, and tetrahydroborato derivatives

The alkyl, aryl, or alkynyl compounds of the form Cp_2LnR exist primarily in configurations related to 4 or 11 because of the need for coordinative saturation. Several examples of both are in the literature, and we can now add $Cp_2^*SmPh(THF)$ to the list. A number of new electron-deficient species, as in 4, will also be revealed.

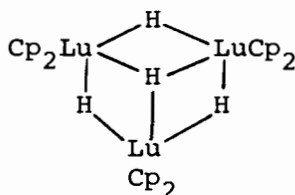


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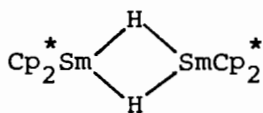
Some of the most exciting advances have occurred in the area of hydride chemistry. We have demonstrated three types of hydride bridged complexes, 12–14, and new examples of these are now available. Since the hydride chemistry of the transition metals is rather well-developed, numerous comparisons can be made. Particular emphasis will be placed on the relation of 14 to Cp_2ML_2 complexes where M = transition metal. The molecule in 14 exhibits a near



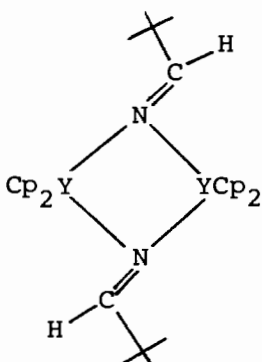
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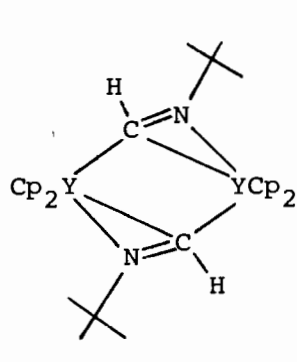
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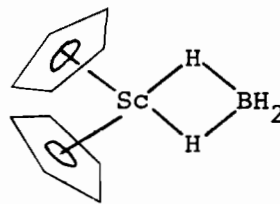


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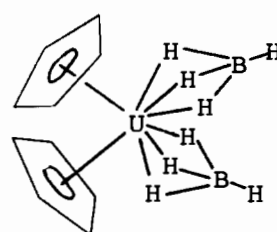
perfect S_4 axis which passes through the two Sm atoms. The dilemma this poses for both crystallographers and theoreticians will be dwelt on.

Evans has just reported some of the novel reactivity of the hydrides with nitriles and isonitriles. Complexes such as 15 and 16 result, and will be discussed in detail. Both the chemistry and the structures can be related to transition metal complexes, but have no true counterparts.

The question of the ligation of the BH_4^- unit is on firmer ground because of two new, accurate structures. $Cp_2^*Sc[BH_4]$ shows the bidentate mode of attachment, 17, while $Cp_2^*U[BH_4]_2$ exhibits tridentate bonding, 18. Structurally, these are similar to the hydride complexes in some respects.



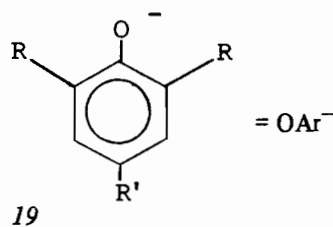
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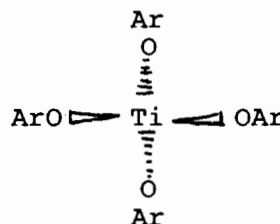
Alkoxy derivatives

One of the fastest developing areas of endeavor involves the use of bulky alkoxydes to stabilize low coordination number lanthanide and actinide complexes. Lappert has pioneered the use of ligands based on 19. While the aromatic backbone is not necessary,

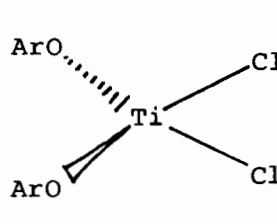


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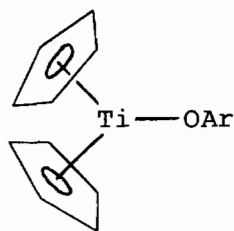
all our structural work to date has involved 19. In unpublished work we have noted the flexibility of 19 with regard to Ti complexes. Three of note are given as 20–22. With 20 and 21, Ti–O–C(Ar) angles of 164–175° are found. In the less crowded 22, the angle drops to 142°. We will discuss this comparison for uranium complexes, and also note the more



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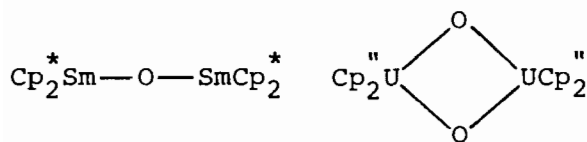
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subtle differences found with the variation in size of the R groups in 19.

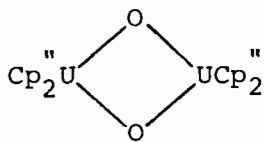
Data is already available for $\text{Cp}_2''\text{U}(\text{OAr})_2$. The U-O distances are short, 2.115(6) Å, and the U-O-C(Ar) angles are 158 and 165°. X-ray data collection is in progress on $\text{U}(\text{OAr})_4$, and the results should be in-hand presently.

Miscellaneous compounds

The ones listed under this heading today may give rise to a new systematic chemistry tomorrow. Some of the most intriguing structural types are the new bridging oxo-complexes. The single oxygen-bridged species, 23, prepared by Evans and co-



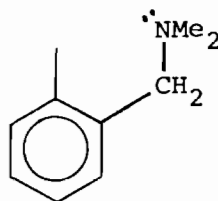
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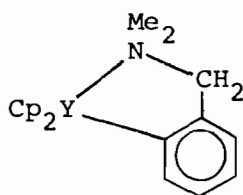
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workers exhibits perfect S_4 symmetry about the Sm-O-Sm vector. The Sm-O length, 2.094(1) Å, is quite short. The apparent origin of the compound is found in the reaction of $\text{Cp}_2^*\text{Sm}(\text{THF})_2$ with NO, and the result is without precedent in transition metal chemistry. The novel 24 shows short U-O lengths, 2.15 Å, but is of unknown origin.

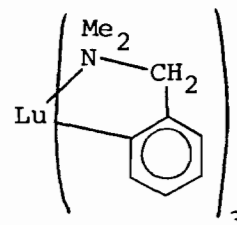
The chelating ligand, 25, first used by Manzer in early transition metal chemistry has given rise to two types of compounds, 26 and 27. In 27, the Lu-C



25



26



27

lengths range narrowly from 2.425(7) to 2.455(7) Å. While the Lu-N distances show a substantial variation, 2.468(6) to 2.588(5) Å. For 26, both distances are on the short end of the spread.

The new material presented is meant to show the diversity of structural types currently available. Organolanthanide and -actinide chemistry has evolved far indeed from the single Cp derivatives of just a few years ago. Comparisons with transition metal counterparts are now interesting and instructive.

We have been fortunate to have longstanding productive collaborations with the synthetic groups of W. J. Evans, M. F. Lappert, M. D. Rausch and M. Tsutsui. Recently, it has been our pleasure to work on structures with the groups of G. Deacon, H. Schumann, and A. Wayda. Without the vast range of compounds from these skilled hands and clever minds, the bright future graphically demonstrated by the structures listed above would not exist. We are grateful to the U.S. National Science Foundation for support of this work.