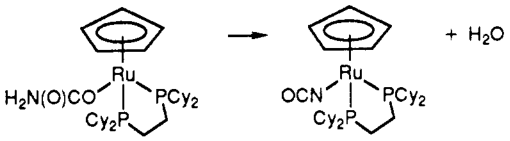
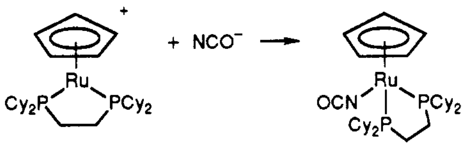
of the carbamate complex slowly convert to a second complex, which is characterized by a single $^{31}P\{^1H\}$ NMR resonance at δ 83.9 and by IR bands at 2238 and 1260 cm^{-1}. These spectral data show that the carbamate complex has been converted to the isocyanate complex via a dehydration reaction (eq 18).[27] The proposed pathway for this



(18)

transformation is shown in Scheme VI. As final confirmation of the stoichiometry of this isocyanate complex, we have independently synthesized it by treating [η^5-cpRu(dcpe)]$^+$ with the isocyanate ion (eq 19).



(19)

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Supplementary Material Available: Tables of positional parameters, bond distances and angles, general displacement parameter expressions, and root-mean-square amplitudes of anisotropic displacement for 14 (14 pages); a table of observed and calculated structure factors for 14 (74 pages). Ordering information is given on any current masthead page.

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(26) Stable complexes are readily obtained by the insertion of carbon dioxide into the metal–nitrogen bond of complexes of substituted amides. For examples see: Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138–46. Tsuda, T.; Watanabe, K.; Miyata, K.; Yamamoto, H.; Saegusa, T. *Inorg. Chem.* 1981, *20*, 2728–30.

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Laser Desorption Fourier Transform Mass Spectrometric Analysis of Organoactinides: Uranium and Thorium Polypyrazolylborates

Zhenmin Liang[†,‡] and Alan G. Marshall*[,†,§]

Departments of Chemistry and Biochemistry, The Ohio State University,
120 West 18th Avenue, Columbus, Ohio 43210

Joaquim Marçalo, Noémia Marques, Antônio Pires de Matos,* and Isabel Santos

Departamento de Quimica, ICEN, LNETI, 2686 Sacavem Codex, Portugal

David A. Weil[‖]

Extrel FTMS, 6416 Schroeder Road, Madison, Wisconsin 53711-2424

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In this work, we report a study of the analytical capabilities of laser desorption Fourier transform ion cyclotron resonance mass spectrometry for the characterization of several air- and moisture-sensitive organoactinide compounds: polypyrazolylborates of uranium and thorium, $AnCl_3[HB(3,5\text{-}Me_2Pz)_3]\cdot THF$, $UCl_2(HBPz_3)_2$, and $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$ (An = Th, U; Pz = pyrazolyl; $x = 1, 2, \ldots$). Although the main focus of this paper is to demonstrate the analytical capability of the technique for detecting intact molecular ions of air-sensitive actinide compounds, some additional structural information can be obtained directly from the positive and negative ion mass spectra. Several interesting new species (for example, dinuclear species of the type $An_2Cl_9^-$ (An = Th, U)) were identified from reactions of laser-formed ions with desorbed neutrals and fragments. Correlations can be made between gas-phase ion-molecule reactions and their counterparts in the condensed phase. In particular, we find that the ionic size of the central metal atom can determine the fragmentation and ion-molecule reaction products.

Introduction

Structural characterization of organic molecules, coordination compounds, and organometallic complexes has recently been greatly facilitated by use of laser desorption/ionization techniques: *l*aser *m*icroprobe *m*ass *s*pectrometry (LMMS)[1] based on time-of-flight mass analysis and *l*aser *d*esorption Fourier transform ion cyclotron resonance *m*ass *s*pectrometry (LD/MS).[2,3] Of the two mass analysis methods, FT/ICR mass spectrometry offers vastly higher mass resolving power (e.g., factor of ~1000

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* To whom correspondence may be addressed.

[†] Department of Chemistry.

[‡] Present address: Extrel FTMS, 6416 Schroeder Road, Madison, WI 53711-2424.

[§] Department of Biochemistry.

[‖] Present address: 3M Corporate Research, 201 BW 09, St. Paul, MN 55144-1000.

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at mass-to-charge ratio $m/z \leq 1000$ or so) and is clearly preferable for compounds with $m/z \leq 5000$. For example, LD with FT/ICR detection has proved successful for analysis of transition-metal organometallic complexes,[4] as well as porphyrins[5,6] and chlorophylls.[7]

On the basis of successful preliminary LD/MS results on a polypyrazolylborate complex of uranium,[8] we decided to study other polypyrazolylborates of uranium and thorium. The polypyrazolylborate ligands $(HBPz_3)^-$ and $[HB(3,5\text{-}Me_2Pz)_3]^-$ have been used as stabilizing ligands in the synthesis of organo compounds of uranium(III) and -(IV) and thorium(IV) and can be considered as alternative ligands to the cyclopentadienyls and substituted cyclopentadienyls. The compounds based on the "$An(HBPz_3)_2$" and "$An[HB(3,5\text{-}Me_2Pz)_3]$" moieties show a very rich chemistry; several such complexes, including amides, alkoxides and aryloxides, thiolates, cyclopentadienides, and σ-hydrocarbyls as additional ligands, have recently been prepared.[9] These air- and moisture-sensitive compounds have been characterized by C, H, N, Cl, and metal elemental analysis, infrared, UV/IR/near-IR, and NMR spectroscopies, and (when crystals were available) single-crystal X-ray diffraction.

Preliminary LD/MS studies[8] of $UCl_3[HB(3,5\text{-}Me_2Pz)_3]\cdot THF$ indicated B–N bond breaking with the formation of the interesting highly coordinatively unsaturated uranium species $[UCl_3(3,5\text{-}Me_2Pz)]^-$. Such B–N bond breaking had already been observed in solution. This finding as well as evidence for a dinuclear species of the type $U_2Cl_9^-$ (see below) may reveal novel synthetic pathways and reactions with direct analogues in solution chemistry of such organoactinide compounds. In order to explore these potentialities, we report in this paper the LD/MS analysis of the analogous thorium compound, the uranium(III) compound $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$, and the unmethylated polypyrazolylborate $UCl_2(HBPz_3)_2$.

Experimental Section

All of the analyzed compounds were synthesized as described previously.[9] Due to their sensitivity to oxygen and moisture, they were handled in inert-atmosphere gloveboxes or by a combination of vacuum and Schlenk techniques. The following compounds were studied: $ThCl_3[HB(3,5\text{-}Me_2Pz)_3\cdot THF$, $UCl_2(HBPz_3)_2$, and $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$ (Pz = pyrazolyl = $C_3H_3N_2$). x is unknown, since no crystals could be obtained. The compound was therefore characterized by C, H, N, Cl, and U elemental analysis and electronic, infrared, and ^1H and ^{11}B NMR spectroscopies. A few milligrams of each compound was dissolved in a few microliters of purified tetrahydrofuran, the sample was transfered to a dimple or groove in a disk-shaped stainless steel probe tip, and the solvent was allowed to evaporate. All of the manipulations were made in a dry argon glovebag. The probe tip was transferred promptly to the mass spectrometer with minimal exposure to the atmosphere.

LD FT/ICR mass spectra were obtained with Extrel FTMS-2000 instruments interfaced either to a Tachisto high-power pulsed CO_2 (10.6-μm) laser (Madison, WI) or a Continuum (formerly Quantel) Model YG600A Nd:YAG (1.064 μm) laser (Columbus, OH). Each positive or negative ion mass spectrum was obtained from a single laser shot, and data were acquired on the source side of a dual ion source/analyzer ion trap.

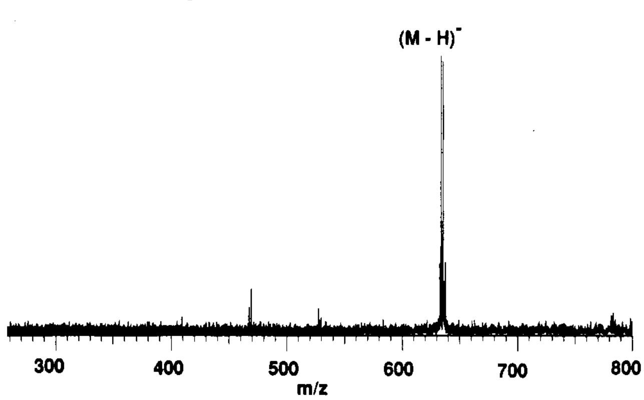

Figure 1. Negative ion Nd:YAG (1.064-μm) LD FT/ICR mass spectrum of $ThCl_3L'\cdot THF$. Note the loss of THF and a proton to leave the predominant ion $[ThCl_3L' - H]^-$.

Table I. Species from the Negative Ion LD FT/ICR Mass Spectra of $AnCl_3L'\bullet THF$ (An = Th, U; L' = $HB(3,5\text{-}Me_2Pz)_3$; Pz = Pyrazolyl)

M = $ThCl_3L'$	M = UCl_3L'[a]
$ThCl_5^-$	UCl_5^-
$ThCl_3(3,5\text{-}Me_2Pz)_2^-$	$UCl_3(3,5\text{-}Me_2Pz)^-$
$[M - H]^-$	$[M]^-$
$[M - H + NH_2]^-$	
$[M + Cl]^-$	
$[M - H + C_2H_6N]^-$	
$Th_2Cl_9^-$	$U_2Cl_9^-$

[a] Data from ref 8.

For LD FT/ICR mass spectra obtained on the Columbus instrument, the operating pressure in the ion trap was ~3 × 10^{-8} Torr. Each laser pulse produced ~30 mJ at the fundamental 1.064-μm wavelength. Synchronization between warmup and Q-switched laser pulses and the FT/ICR experimental event sequence is described elsewhere.[10] The highest ion yield was obtained when ions generated from a given laser pulse were allowed to pass into the ion trap by grounding the source trap plate for 2 ms after the laser pulse, after which the trapping potential was raised to 2 V and left there for ~2 s to provide an ion thermalization and/or ion-molecule reaction period. The effect of trap voltage gating on ion trapping efficiency is discussed elsewhere.[11] Coherent ion cyclotron motion was then excited by frequency-swept irradiation over a bandwidth extending from dc to several hundred kilohertz to 1 MHz at a sweep rate of a few hundred hertz per microsecond at an rf amplitude of ~10 dB below 130 V (p-p). Direct-mode detection over the same bandwidth generated either 32K (or 64K) time-domain data, to which another 32K (or 64K) zeros were added before discrete Fourier transformation. No time-domain windowing was employed.

Detection conditions for the CO_2 LD/MS experiments carried out in Madison were similar, except for higher sweep rate (1 kHz/μs) and wider mass range. The output energy of the laser was controlled by adjusting an aperture and was estimated to be ~0.05 J per pulse for the laser desorption/ionization experiments. In the Madison experiments, the source trap electrode was grounded for 100 μs after the laser pulse, after which the trapping potential was raised to 1 V for positive ion and −1 V for negative ion detection.

Results and Discussion

$ThCl_3L'\cdot THF$ (L' = $HB(3,5\text{-}Me_3Pz)_3$). The negative ion Nd:YAG LD mass spectrum of this compound (Figure

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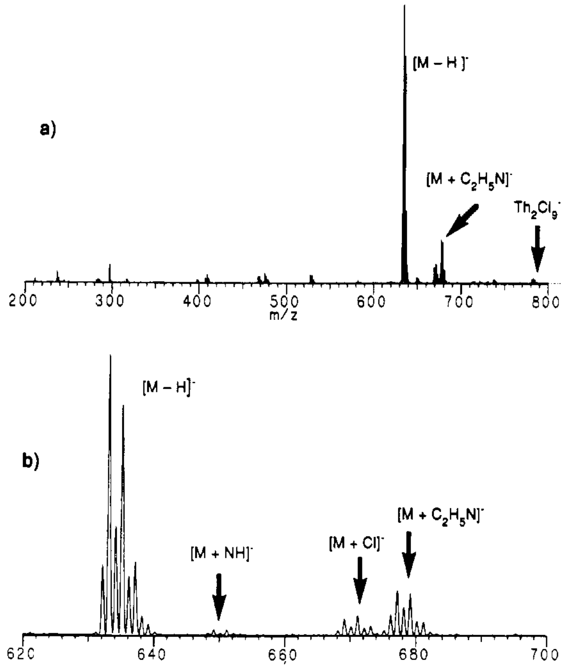

Figure 2. Negative ion CO_2 (10.6-μm) LD FT/ICR mass spectrum of the same compound as in Figure 1: (a) wide-range mass spectrum; (b) higher resolution display of a selected spectral segment. Note the increased degree of fragmentation as well as ion–molecule reactions to produce species of mass higher than the parent compound.

Table II. Species from the Positive Ion LD FT/ICR Mass Spectra of $AnCl_3L' \bullet THF$ (An = Th, U; L′ = $HB(3,5\text{-}Me_2Pz)_3$; Pz = Pyrazolyl)

M = $ThCl_3L'$	M = UCl_3L'[a]
$ThCl_2L'^+$	$UCl_2L'^+$
	$[M]^+$
$[M + Na]^+$	$[M + Na]^+$ (?)
$[M + K]^+$	$[M + K]^+$
$[M + Na + K]^+$	$[M + Na + K]^+$

[a] Data from ref 8.

1) exhibits very little fragmentation. Loss of THF and a proton from the neutral parent yields the most abundant ionic species, $[ThCl_3L' - H]^-$. The same experiment conducted with a CO_2 laser (Figure 2) produces considerably more fragmentation (perhaps due to greater sample heating by the laser pulse) as well as higher mass species due to further ion–molecule reactions. Isotopic relative abundances are especially helpful in assigning species containing boron and chlorine atoms, as shown nicely in Figure 2b.

The analogous uranium compound has previously been analyzed by Bjarnason et al.[8] The results obtained for the uranium and thorium negative ions are compared in Table I. Positive ion LD mass spectra (not shown) have been obtained for the homologous uranium and thorium compounds. Table II lists assignments for the major ionic species.

In all of the above LD mass spectra, no coordinated THF could be observed, in accord with the lability of this ligand in the case of the uranium compound, which can also be prepared without a coordinated THF.[9a] All attempts to prepare the adduct-free thorium compound failed: it appears that this species can be prepared only in the gas phase.

As seen from Table I, B–N bond breaking of the pyrazolylborate ligand is clearly observed, and the fragment ions $ThCl_3(3,5\text{-}Me_2Pz)_2^-$ (m/z = 527) and $UCl_3(3,5\text{-}Me_2Pz)^-$ (m/z = 438) can be identified. These species are remarkable for their high coordinative unsaturation and probably could not be prepared in solution unless suitable counterions are used or dimers are formed. For example, $ThCl_4$ and UCl_4 in the condensed phase have high coordination numbers due to chlorine bridging. Incidentally, B–N bond breaking has also been observed in solution when UCl_4 is reacted in tetrahydrofuran with 2 equiv of $KHB(3,5\text{-}Me_2Pz)_3$, resulting in the formation of $UCl_2[HB(3,5\text{-}Me_2Pz)_3](3,5\text{-}Me_2Pz)$.[12]

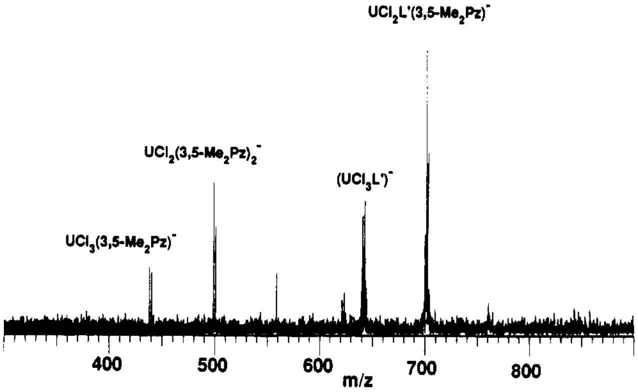

Figure 3. Negative ion Nd:YAG (1.064-μm) LD FT/ICR mass spectrum of $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$ (see text for peak assignments).

The polypyrazolylborate nitrogen donor ligand suffers further fragmentation, as seen from the presence of species with NH_2^- or $C_2H_6N^-$ amide ligands coordinated to the thorium. From Table I, it is evident that the larger ionic size of thorium permits this element to stabilize species with coordination numbers larger than for the corresponding uranium species: compare $ThCl_3(3,5\text{-}Me_2Pz)_2^-$ with $UCl_3(3,5\text{-}Me_2Pz)^-$ and note the species $[M - H + NH_2]^-$, $[M + Cl]^-$, and $[M - H + C_2H_6N]^-$, which are formed only with thorium. Moreover, dinuclear species of the type $An_2Cl_9^-$ (An = Th, U) are clearly identified. The uranium species $U_2Cl_9^-$ has previously been identified in a preliminary phase diagram study of CsU_2Cl_9 by Barton et al.[13] Also, Cotton et al. have prepared the dinuclear uranium alkoxides $KU_2(OCMe_3)_9$, $U_2(OCMe_3)_9$, and $U_2(OCHMe_2)_{10}$.[14]

The positive ion LD mass spectra are less informative, partly because minor contamination by sodium and potassium (which we suspect are always present in small quantity due to the synthetic processes used) yielded pseudomolecular ions of the type $(M + K)^+$ and $(M + Na)^+$. The molecular ion $[M]^+$ is formed only for the uranium compound, since the corresponding thorium $[M]^+$ ion would require a Th(V) oxidation state. Interestingly, the coordinatively unsaturated species $AnCl_2L'^+$ is obtained for both An = U and Th.

$\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$. The following species may be identified from the negative ion LD mass spectrum shown in Figure 3:

m/z	
438	$UCl_3(3,5\text{-}Me_2Pz)^-$
498	$UCl_2(3,5\text{-}Me_2Pz)_2^-$
640	$UCl_3L'^-$
700	$UCl_2L'(3,5\text{-}Me_2Pz)^-$
760	$UClL'(3,5\text{-}Me_2Pz)_2^-$

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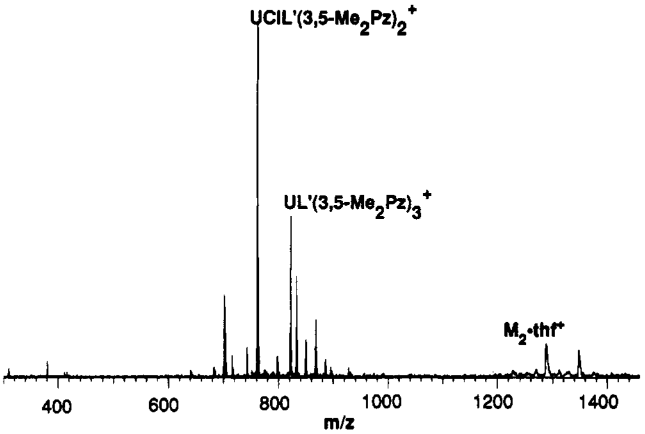


Figure 4. Positive ion Nd:YAG (1.064-μm) LD FT/ICR mass spectrum of $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$ (see text for peak assignments). Note the appearance of the uranium dimer species.

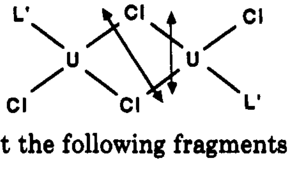
The corresponding positive ion LD mass spectrum is shown in Figure 4. This spectrum shows many more fragments, and the following tentative assignments can be made:

m/z	
700	$UCl_2L'(3,5\text{-}Me_2Pz)^+$
760	$UClL'(3,5\text{-}Me_2Pz)_2^+$
820	$UL'(3,5\text{-}Me_2Pz)_3^+$

It is interesting that THF adducts are observed in the positive ion mass spectrum ($UClL'(3,5\text{-}Me_2Pz)_2{\cdot}THF^+$ at *m/z* 832, $UCl_2L'(3,5\text{-}Me_2Pz)_2{\cdot}THF^+$ and $[M]_2{\cdot}THF^+$ (*m/z* 1287, with centroid at *m/z* 1284)) but not in the negative ion mass spectrum.

Although Santos[9f] had previously found some evidence that the uranium(III) compound might be a dimer, no dimer was observed in the mass spectrum. However, in the positive ion LD mass spectrum, we can tentatively assign the peak at *m/z* = 1287: since the sample was dissolved in tetrahydrofuran, it is possible that the THF ligand bridges two monomers. The related uranium(III) compound $(UCp_3)_2$(pyrazine) has been studied by Eigenbrot[15] by mass spectrometry. Although the molecular species, a dimer confirmed by X-ray diffraction, was not observed, dinuclear species showing loss of one, two, or three Cp ligands were observed in the mass spectrum.

As for the previously described uranium and thorium compounds, B–N bond breaking was observed and pyrazolide ligands were found attached to the metal; the species $UCl_3(3,5\text{-}Me_2Pz)^-$ and $UCl_3L'^-$ appeared as previously noted for the negative ion LD mass spectrum of the uranium(IV) compound $UCl_3[HB(3,5\text{-}Me_2Pz)_3]{\cdot}THF$. For the proposed dimer



one might expect the following fragments to result from laser desorption: UCl_3L', $UClL'$, and UCl_2L'. The last two species would be expected to have short lifetimes because of their high coordinative unsaturation. As we have verified above, B–N bond breaking of the L' ligand gave rise to $3,5\text{-}Me_2Pz$ fragments which would be expected to react further with the ionic species present. Finally, it is interesting to note Santos[9f] observed that, in solution, the complex $(UCl_2L')_x$ reacts with $CHCl_3$, giving the species UCl_3L' and $UCl_2L'(3,5\text{-}Me_2Pz)$.

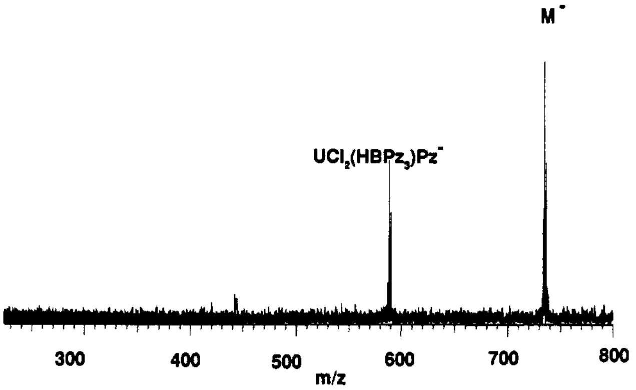


Figure 5. Negative ion Nd:YAG (1.064-μm) LD FT/ICR mass spectrum of $UCl_2(HBPz_3)_2$. Note the prominent molecular ion peak.

$UCl_2(HBPz_3)_2$. This compound is more coordinatively saturated than the other three compounds just described. Figure 5 shows the negative ion LD mass spectrum, which exhibits much less fragmentation than those previously discussed. The most prominent peak is due to the molecular ion, $UCl_2(HBPz_3)_2^-$. The only other prominent peak can be assigned to $UCl_2(HBPz_3)Pz^-$, indicating B–N bond breaking of the ligand $HBPz_3^-$. These results are consistent with a higher stability for the title compound.

Conclusions

In this work, we have demonstrated that laser desorption Fourier transform mass spectrometry is a powerful analytical method for the identification and characterization of air-sensitive organoactinide compounds. The gas-phase synthesis of new organo compounds reveals novel synthetic pathways and reactions that appear to be related to the solution chemistry. For example, evidence for B–N bond breaking was demonstrated, leading to new pyrazolide complexes that may also be prepared in solution. Also, our observation of stable gas-phase dinuclear ionic species of the type $An_2Cl_9^-$ may lead to the synthesis of new ionic or neutral dinuclear compounds in solution. Moreover, the observation of stable $UCl_2(HBPz_3)Pz^-$ in Figure 5 offers encouragement for attempts to prepare the coordinatively unsaturated neutral compound $UCl_2(HBPz_3)Pz$. A final interesting result is the influence of the ionic size of the central ion, demonstrated by the ability of the thorium to form species with higher coordination numbers.

Acknowledgment. This work was made possible by grants from the U.S. National Science Foundation (Grant No. CHE-87-21498 (A.G.M.)) and Fundação Luso-Americana (A.P.M.).

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