

COMPARISON OF YTTRIUM, LANTHANIDES AND ACTINIDES IN RESPECT TO UNIT CELL VOLUMES OF ISOSTRUCTURAL COMPOUNDS AND THERMODYNAMIC FUNCTIONS OF COMPLEX FORMATION

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The investigations carried out till now and presented in this paper show that apart from the well known itinerant properties of yttrium in respect to free energy of complex formation, also actinides(III) change their position in the lanthanide series in respect to ΔG . It has also been shown that yttrium and actinides exhibit itinerant behaviour in respect to unit cell volumes. Evidence has been presented that delocalization of 4f and 5f orbitals is the reason for the two types of migratory properties. Since the itinerant behaviour of yttrium and actinides(III) in respect to stability constants (free energies of complex formation) is the basis for yttrium-lanthanides and lanthanides-actinides group separations, a better qualitative understanding of the mechanism involved may contribute to the development of more efficient separation procedures.

Introduction

Yttrium, lanthanides and actinides are very similar elements in respect to many properties but show also remarkable differences, which are bases for many group separation procedures. Thus, procedures aimed at the separation of yttrium from lanthanides are based on the ability of yttrium to change its position in the lanthanide series with the change of the ligand. Apparently, the same is also valid for actinides(III) and makes possible to separate heavy actinides from lanthanides. It is very probable that the itinerant character of yttrium and actinides(III) is due to the ligand-dependent delocalization of 4f and 5f orbitals. In order to check this presumption, the position of yttrium and actinides in the lanthanide series with respect to unit cell volumes of isostructural compounds and thermodynamic functions of complex formation has been studied in this Department. The present paper is a summary of results obtained till now.¹⁻⁶

The position of yttrium or an actinide in the lanthanide series with respect to a given property, P, can be quantitatively specified by a relative or apparent atomic

number, $Z_M(P)$. This number can be calculated from the following expression based on linear interpolation

$$Z_M(P) = Z_{Ln'} + \frac{P_{Ln'} - P_M}{P_{Ln''} - P_{Ln'}} \quad (1)$$

where M denotes yttrium or an actinide, P stands either for unit cell volume or for ΔG° , ΔH° and ΔS° of complex formation, and Ln' and Ln'' are two lanthanides encompassing yttrium or the actinide, $Z_{Ln'} < Z_{Ln''}$. The itinerant properties of yttrium and actinides are reflected in changes of $Z_M(P)$ which, in general, is not a whole number.

Results and discussion

Unit cell volumes

The unit cell volumes of isostructural yttrium, lanthanide and actinide M_mX_n compounds were calculated from published data. The apparent atomic numbers of yttrium and actinides from Ac to Cf, except for Th and Pa, were

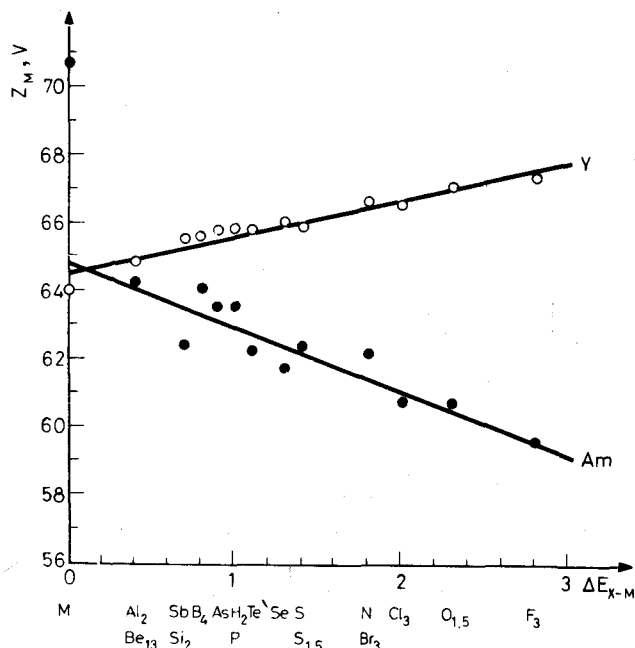


Fig. 1. The position of yttrium and americium in the lanthanide series in respect to unit cell volumes as a function of the electronegativity of the X atom in the isostructural M_mX_n compounds

then calculated from Eq. (1) and plotted against the difference between the electronegativity of the X and Ln atoms. Figure 1 presents such a plot for yttrium and americium, and Fig. 2 summarizes the results obtained for all the actinides studied, except for actinium. It was assumed that the difference in electronegativity, ΔE_{X-M} , may serve as a rough measure of the tendency of the M and X atoms to form covalent bonding. Actinium in all its compounds falls out of the lanthanide series, so that $Z_{Ac}(V)$ could be only very approximately estimated by extrapolating unit cell volumes of the respective lanthanide compounds to atomic numbers smaller than 57. It follows from the few data available that actinium practically does not change its position in the lanthanide series. It is seen from Fig. 2 that $Z_Y(V)$ increases with increasing electronegativity, whereas the apparent atomic numbers of actinides, except for actinium, decrease with increasing electronegativity. The results obtained can be qualitatively explained by the following considerations. Let us assume that there is a contribution of f-orbitals to bonding, greater for 4f than for 5f orbitals. If so, then the covalency shortening of bonds and the resulting decrease in the unit cell volumes of isostructural compounds is greater for actinides than for lanthanides. Since unit cell volumes of lanthanide compounds decrease with increasing lanthanide atomic number, the inclusion of covalency and the accompanying decrease in unit cell volumes, greater for actinides than for lanthanides, shifts $Z_{An}(V)$ towards higher values. Therefore, for compounds with high contribution of covalency to bonding such as intermetallics, actinides are heavy pseudolanthanides, whereas for purely ionic compounds like fluorides, actinides resemble light lanthanides. In the case of yttrium there is no contribution from covalency to bonding due f-orbitals, so that $Z_Y(V)$ decreases with increasing delocalization of 4f orbitals in lanthanide compounds.

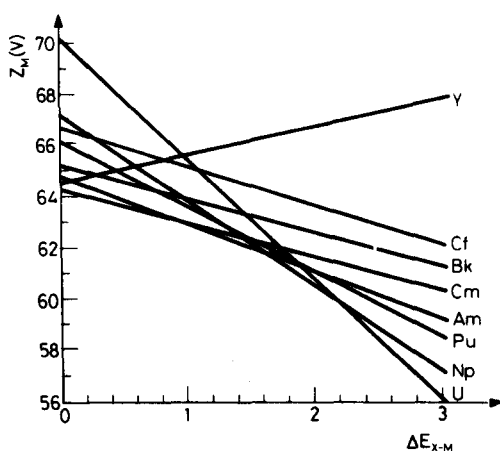


Fig. 2. Comparison of results obtained for different actinides. $Z_{An}(V)$ as a function of the electronegativity of the X atom

Thermodynamic functions of complex formation

The position of yttrium, actinium, plutonium(III) and americium(III) in the lanthanide series in respect to ΔG° , ΔH° and ΔS° of complex formation with nitrates, and thiocyanates was studied. It was assumed that for the hard nitrate ligand the metal-ligand bond should be completely ionic, whereas in the case of a soft thiocyanate ligand a considerable contribution from covalency to bonding should be present. The thermodynamic functions of complex formation were calculated from stability constants and their changes with temperature. Stability constants at different temperatures were, in turn, determined from extraction experiments. It was shown that under certain simplifying assumptions, stability constants of complexes with nitrates and thiocyanates are proportional to the respective distribution ratios. In case of the nitrate ligand the system studied was 20% w/v Adogen-464 NO_3 in xylene and 3M NH_4NO_3 . The thermodynamic functions of complex formation refer to β_5 stability constants. In case of the thiocyanate ligand the system studied was 0.2M TBP in heptane and 3M NaSCN , and the thermodynamic functions refer to β_3 stability constants. From the ΔG , ΔH and ΔS values determined for yttrium, lanthanides and the actinides(III) studied the three relative atomic numbers of yttrium and actinides ($Z_M(\text{G})$, $Z_M(\text{H})$, $Z_M(\text{S})$) were calculated using Eq. (1). The results are shown in Table 1. Figure 3 presents the position of plutonium and americium in the lanthanide series for the thiocyanate system.

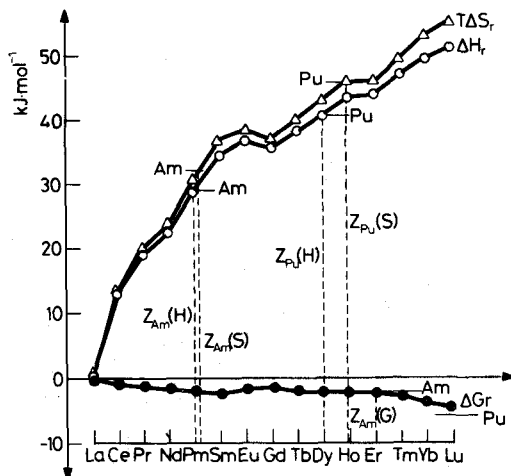


Fig. 3. The relative atomic numbers of Pu(III) and Am(III) in respect to ΔG° , ΔH° and ΔS° of complex formation. Extraction with 0.2 M TBP in heptane from 3M NaSCN

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Table 1
Relative atomic numbers of Y, Ac(III), Pu(III), Am(III) and Cm(III)
for nitrate and thiocyanate ligands

Element	Nitrates			Thiocyanates		
	$Z_M(G)$	$Z_M(H)$	$Z_M(S)$	$Z_M(G)$	$Z_M(H)$	$Z_M(S)$
Y	69.5	69.5	69.5	57.5	>71	71.0
Ac	58.1	58.1	58.1	<57	58.4	57.9
Pu	58.9	58.9	58.9	71	66.0	66.8
Am	59.8	59.8	59.8	68.0	61.0	61.2
Cm	60.4	60.4	60.4	—	—	—

It is seen from Table 1 that in the nitrate system the equality $Z_M(G) = Z_M(H) = Z_M(S)$ is valid for both yttrium and actinides. In the nitrate system yttrium is a heavy pseudolanthanide, whereas actinides are light or medium pseudolanthanides in respect to each ΔG , ΔH and ΔS of complex formation. The apparent atomic numbers of the actinides studied till now increase slightly with decreasing actinide ionic radius.

In case of the thiocyanate system the difference $Z_M(H) - Z_M(S)$ is positive for yttrium and actinium and negative for Pu(III) and Am(III). Since ΔH and ΔS for lanthanides increase with Z and ΔG decreases with increasing Z , a negative value of the difference $Z_M(H) - Z_M(S)$ means a low value of $Z_M(G)$, and a positive value means a high value of $Z_M(G)$. Therefore, in the thiocyanate system yttrium and actinium are light pseudolanthanide, whereas plutonium(III) and americium(III) are heavy pseudolanthanides in respect to ΔG . It is interesting to notice that for the three actinides studied the change in each apparent atomic number $Z_M(G)$, $Z_M(H)$ and $Z_M(S)$ is inversed to the change in the actinide metallic radius, which decreases between Ac and Pu and increases between Pu and Am.

A comparison of the two complexing ligands reveals a striking similarity between the itinerant behaviour of yttrium and actinides with respect to unit cell volumes of isostructural compounds and to free energy of complex formation. Thus, for the hard nitrate ligand and for highly electronegative counteratoms like fluorine or oxygen, yttrium is a heavy pseudolanthanide, whereas plutonium, americium and curium are light pseudolanthanides. For the soft thiocyanate ligand and for counteratoms of low electronegativity values as in intermetallic compounds the reversed behaviour is observed. The itinerant properties of yttrium and actinides with respect to unit cell volumes can be explained by a contribution from covalency to bonding and by the resulting covalency shortening, both increasing in the order $Y < \text{lanthanides} < \text{actinides}$. Because of the observed similarity, the itinerant behaviour with respect to

ΔG of complex formation may have the same origin. Inclusion of covalency due to the delocalization of f-orbitals, greater for actinides than for lanthanides and absent for yttrium, results in a metal-ligand bond shortening greater for actinides than for lanthanides. This bond shortening results in a change of enthalpy and entropy of complex formation. However, comparison of the enthalpic with the entropic position of yttrium and the respective positions of actinides in the thiocyanate system shows that enthalpy and entropy of complex formation are influenced by the bond shortening to a different degree, $Z_M(H) - Z_M(S) \neq 0$. The positive value of the $Z_M(H) - Z_M(S)$ difference in the case of yttrium and the negative value of this difference in the case of plutonium(III) and americium(III) result in a considerable decrease of $Z_Y(G)$ and increase of $Z_{Pu}(G)$ and $Z_{Am}(G)$ in the thiocyanate system, in comparison to the nitrate system. It should be noted that actinium behaves similarly to yttrium, which means that actinium 5f orbitals are not delocalized in the actinium thiocyanate complex.

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