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Mixed condensed f-element clusters *

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Abstract

Mixed condensed Gd_2Cl_3-type clusters for actinides (Pa, Np, Pu, Cm, Bk) and some lanthanides were studied and interesting results were obtained.

Keywords: f-Elements; Lanthanide clusters

1. Introduction

Much attention has been paid to the study of lanthanide clusters in works by Simon and coworkers [1–3]. They obtained a number of compounds of these elements in which the oxidation states of the lanthanides change from 1.0 to 2.0. The greater part of the clusters synthesized by these authors was obtained by the solid synthesis technique. However, of special interest are the compounds of type MX and M_2X_3 obtained through interaction of metal with the melt of the respective trihalide. Thorough investigations showed that these compounds represent so-called condensed clusters, whose structures and properties are considered in greater detail in reviews [2,3]. Analogous compounds for the actinide elements are so far unknown.

Clusters of this type were obtained for Gd, Lu, Tb, Y and other elements.

From the point of view of coordination chemistry, the possibility of substitution of separate metal atoms, forming a condensed cluster, by the atoms of another metal with similar properties, i.e. the possibility of the formation of mixed clusters, seems very promising. This problem first arose in [4,5] during study of the cocrystallization of various elements with Gd_2Cl_3.

2. Results and discussion

From the works of Simon and coworkers, it follows that some lanthanides are not able to form condensed clusters through interaction of their melts with a molten trihalide. Eu, Sm, Yb and other elements belong to this group. This may imply that synthesis does not provide the conditions for the solid phase of the cluster to be formed. However, this does not imply that the formation of clusters by the above elements is impossible in principle. If it is so, the lanthanide in question must take part in cocrystallization during the formation of a matrix, e.g. Gd_2Cl_3.

As was mentioned above, the formation of Gd_2Cl_3 occurs through interaction of metallic Gd with $GdCl_3$ at a temperature close to the melting point of $GdCl_3$. Corbett showed that under these conditions Gd dissolves partially in $GdCl_3$, its solubility being about 2 mol% at 883 K. It was established in [6] that dissolution of Gd is accompanied by the formation of Gd^{2+} ions. Thus a redox system is formed, where in the presence of $GdCl_3$ in the melt, the lanthanides and actinides will be reduced to the oxidation state 2+ with the degree of reduction depending on their standard oxidation potentials (Table 1). As is shown in Table 1, some lanthanides and actinides are reduced almost completely to their divalent states, some are reduced partially, and some remain in the oxidation state 3+. As was mentioned above, f-elements in the divalent state may be subdivided into two types depending on their electron configuration.

Three problems were to be solved during study of the cocrystallization of these elements with Gd_2Cl_3:

(1) whether the lanthanides and actinides can cocrystallize with Gd_2Cl_3, if they have an f^nd^0 configuration in the divalent state;

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Table 1
The ratio of M^{3+} to M^{2+} in the system Gd^0–$GdCl_3$ at 883 K [7]

Element	$E^0_{M3+/M2+}$ (V)	$[M^{3+}]/[M^{2+}]$
Lanthanide		
La	−2.94	51
Ce	−2.92	39
Pr	−2.84	14
Nd	−2.62	0.76
Pm	−2.44	0.072
Sm	−1.5	3.1×10^{-5}
Eu	−0.34	6.2×10^{-14}
Gd	−2.85	16
Tb	−2.83	12
Dy	−2.56	0.35
Ho	−2.79	7.1
Er	−2.87	20
Tm	−2.22	0.004
Yb	−1.18	4.6×10^{-9}
Lu	−2.72	2.8
Actinide		
Pa	−2.59	0.535
U	−2.54	0.27
Np	−2.91	34
Pu	−2.59	0.51
Am	−2.28	0.0087
Cm	−2.78	6.2
Bk	−2.52	0.214
Cf	−1.63	3.5×10^{-5}
d-element		
Y	−2.92	39

Table 2
Distribution of Ln and An during cocrystallization with Gd_2Cl_3 in the system Gd^0–$GdCl_3$ [7,9–11]

M	Electronic configuration M^{2+} in melt	% in Gd_2Cl_3	M	Electronic configuration M^{2+} in melt	% in Gd_2Cl_3
Eu	f^7d^0	2	Ce	f^1d^1	6
Yb	$f^{14}d^0$	2	Tb	f^8d^1	68
Nd	f^4d^0	2	Lu	$f^{14}d^1$	50
Am	f^7d^0	2	Pa	f^2d^1	68
Cf	$f^{10}d^0$	2	U	f^3d^1	46
			Np	f^4d^1	76
			Pu	f^5d^1	38
			Cm	f^7d^1	38
			Bk	f^8d^1	19

(2) whether Ln^{2+} and An^{2+} can cocrystallize with Gd_2Cl_3 if they have an $f^{n-1}d^1$ configuration;

(3) in which oxidation state f-elements cocrystallize with the Gd_2Cl_3 matrix.

The answer to the first question was given in papers [5,7,8] where it was shown that Eu, Yb, Nd, Dy, Tm, Am and Cf did not cocrystallize with Gd_2Cl_3. All these elements in the divalent state had an f^nd^0 electronic configuration. As follows from Table 1, under the conditions of the experiment they are reduced, with a degree of reduction different from the oxidation state 2+. Thus, cocrystallization of these elements occurs neither in the di nor in the trivalent state.

Further studies [8–11] showed that Pa, U, Np, Pu, Cm, Bk, Tb and Y, i.e. elements which in the $GdCl_3$ melt in the form of M^{2+} have an $f^{n-1}d^1$ configuration, cocrystallized with Gd_2Cl_3. Since the degrees of reduction of these elements under the conditions of the experiment are different (Table 1) the question of the valency of Ln and An in cocrystallization remains open. The maximum transition to the Gd_2Cl_3 phase was observed in the case of Np and Tb (Table 2), i.e. as regards the element with the lowest degree of reduction, and vice versa; Pu, having the highest degree of reduction, is incorporated least of all by the Gd_2Cl_3 phase.

For a better understanding of the formation of the Gd_2Cl_3 cluster the authors of [7] considered two mechanisms:

$$\begin{array}{l} Gd^0 + 2GdCl_3 \longrightarrow 3GdCl_2 \\ 3GdCl_2 \longrightarrow Gd_2Cl_3 + GdCl_3 \\ \hline Gd^0 + GdCl_3 \longrightarrow Gd_2Cl_3 \end{array} \qquad (1)$$

$$\begin{array}{c} Gd^0 \longrightarrow Gd^{3+} + 3e^- \\ 2GdCl_3 + 3e^- \longrightarrow Gd_2Cl_3 + 3Cl^- \\ Gd^{3+} + 3Cl^- \longrightarrow GdCl_3 \\ \hline Gd^0 + GdCl_3 \longrightarrow Gd_2Cl_3 \end{array} \qquad (2)$$

For these two cocrystallization equations, taking into account the solubility of metallic Gd^0 in $GdCl_3$ k, the ratio between divalent and trivalent forms of macrocomponents and microcomponents, determined by the $\Delta E^0_{M-\mu}$ value, i.e. by the difference in standard oxidation potentials of the pairs M^{3+}/M^{2+} for Gd (M) and microcomponent (μ), and the distribution of the microcomponent between molten $GdCl_3$ and the solid phase Gd_2Cl_3 λ were obtained:

$$\ln\frac{a}{a-b} = \frac{2(1+k)\exp[\Delta E^0_{M-\mu}/(RT/F)]}{1+k\exp[\Delta E^0_{M-\mu}/(RT/F)]}\cdot\lambda_1\ln\frac{2b}{2b-y} \qquad (3)$$

(first process of cluster formation)

$$\ln\frac{a}{a-x} = \frac{2(1+k)\exp[\Delta E^0_{M-\mu}/(RT/F)]}{1+k\exp[\Delta E^0_{M-\mu}/(RT/F)]}\lambda_2\ln\frac{2b}{2b-y} \qquad (4)$$

(second process of cluster formation)

a and b are the contents of macrocomponents and microcomponents in the system, x and y are their contents in the cluster phase. If $\Delta E^0_{M-\mu}=0$, it follows that

$$\ln \frac{a}{a-x} = 2\lambda \ln \frac{2b}{2b-y} \tag{5}$$

In this case it is impossible to choose between the first and second processes of cluster formation. At the same time, one should pay attention to the fact that the first process implies the existence of divalent Gd. In this case, if the microcomponent, which also reduces to the oxidation state 2+ and has an $f^{n-1}d^1$ electron configuration, is introduced into the system, its cocrystallization ability will be determined by the participation of this element in the divalent state. The second process implies the participation in cocrystallization of the trivalent form of the element, therefore in this case the opposite tendency should be observed, i.e. cocrystallization worsens on increasing the share of the reduced form of the element.

Since we are speaking about elements with similar ionic radii, their cocrystallization coefficients are supposed to be close. Table 3 shows the λ_1 and λ_2 values for the elements in question calculated according to Eqs. (3) and (4) respectively. From these data it follows that only the λ_2 coefficients are in agreement with each other. Therefore, the authors conclude that the process of formation of Gd_2Cl_3 occurs according to the second process, i.e. with the trivalent form of the element participating in cocrystallization.

In addition, as was shown above, the $f^{n-1}d^1$ electronic configuration of the divalent form of the element plays the crucial role in cluster formation.

Table 3
Cocrystallization coefficients of elements with Gd_2Cl_3 [7,9–11]

Element	λ_1	λ_2
Pa	–	2.59
U	–	2.32
Np	1.16	2.21
Pu	0.07	2.03
Cm	0.70	1.73
Bk	–	1.20

Table 4
Dependence of the cocrystallization coefficient (λ_2) on the ionic radius of M^{3+} [8]

Element	$R_{M^{3+}}$ (nm)	λ_2
La	0.1061	0.04
Ce	0.1034	0.1
Pr	0.1013	0.5
Gd	0.0938	–
Tb	0.0923	1.6
Ho	0.0894	1.0
Er	0.0881	1.3
Lu	0.0848	2.5
Y	0.0900	1.9

These conclusions are in agreement with data on the magnetic properties of Gd_2Cl_3, Mössbauer and photoelectron spectroscopy of Gd_2Cl_3 [1] and with the (sp)d-character of additional 1.5 electrons per Gd atom [3]. The presence of the (sp)d-character of additional electrons in the metal atoms of the cluster implies a specific role of d-electrons and the possibility of splitting of the d-level in the ligand field. In this respect, the behavior of Pr, Ho and Er in the process of formation of mixed clusters with Gd_2Cl_3 seems very interesting. These elements in a free state and also in the melt [12] have an f^nd^0 configuration of M^{2+}. However, from their energy parameters they are close to Gd^{2+} and Tb^{2+} having an $f^{n-1}d^1$ configuration [13]. If the ligand field splitting in the solid matrix is assumed to be higher than that in the melt, one may expect the stabilization of Pr, Ho and Er in an $f^{n-1}d^1$ configuration, and consequently the formation of mixed clusters with Gd_2Cl_3 by them. Actually, it appeared that Pr, Ho and Er incorporated in the Gd_2Cl_3 phase with λ_2 coefficients (Eq. (4)) of 0.50, 1.01 and 1.32 respectively. Thus, one may conclude that all these elements cocrystallize owing to their $f^{n-1}d^1$ configurations, stabilizing in the ligand field of the Gd_2Cl_3 matrix.

At the same time, it should be noted that cocrystallization coefficients of Ho and Er differ by more than 2 times from the cocrystallization coefficient of Pr. The cocrystallization of La, Ce, Pr, Y and Lu was studied to determine the effect of the ionic radius on the formation of a mixed cluster. All these elements in their divalent states have an $f^{n-1}d^1$ electronic configuration, except for Y^{2+} which has a [Kr]d^1 configuration. As is shown in Table 4, in this group of elements the ionic radii decrease from La to Lu. Moreover, for the elements with ionic radii smaller than that of Gd^{2+}, the λ_2 value is close to or higher than unity. An increase in the ionic radius of Pr^{3+} by 5.5% as compared with Gd^{3+} decreases λ_2 twofold.

A further increase in the radii of Ce and La results in an abrupt decrease in the cocrystallization of these elements with the Gd_2Cl_3 cluster. Thus, in the system $(Gd,Ln)_2Cl_3$ there is an upper miscibility limit depending on the radius of the near lanthanide elements.

Finally it is to be noted that studies of the chemistry of the actinides and lanthanides with an $f^{n-1}d^1$ configuration show that there is a specific relation and similarity between these elements and trivalent Y, and obviously Sc, which is manifested in their ability to form dimers and condensed clusters.

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