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Enthalpies of Formation of RNi_5 Compounds

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The RNi_5 compounds (with R = La, Ce, Pr, Sm, Y) crystallize in the hexagonal $CaCu_5$ type structure. This close packed stacking is characterized by a cell parameter directly related to the R and Ni atomic radii, $a = \sqrt{3(r_{Ni} + r_R)}$, and by the c parameter which depends almost entirely on the Ni atomic radius, $c = \sqrt{15r_{Ni}(r_{Ni} - 2r_R/15) - r_R^2}$.

The a lattice parameter variation inside the series RNi_5 displays an anomaly for $CeNi_5$ compound [1]. This anomaly has been studied previously by means of magnetic properties and X-ray absorption [2]; the X-ray absorption experiments show that in $CeNi_5$, Ce has the same valence state close to 4^+ as in the insulator CeO_2.

In the present study the enthalpies of formation of the RNi_5 compounds are measured by a calorimetric method. The variation of enthalpies of formation inside the series RNi_5 shows an anomaly for $CeNi_5$ compound; this study allows us to estimate the energy associated to this anomaly.

The enthalpy of formation of the RNi_5 compound corresponds to the reaction:

$$\langle R\rangle_{To} + 5\langle Ni\rangle_{To} \longrightarrow \langle RNi_5\rangle_{To}$$

Its value is deduced from the dissolution enthalpies of the compound and its components in liquid aluminium by using the relation:

$$\Delta H_f^{To}(RNi_5) = Q_R^\infty + 5Q_{Ni}^\infty - Q_{RNi_5}^\infty$$

where Q_x^∞ (x = R, Ni, RNi_5) is the heat of dissolution at infinite dilution of the compound or the elements.

The enthalpies of dissolution were measured using an isoperibolic calorimeter which has been described elsewhere [3,4].

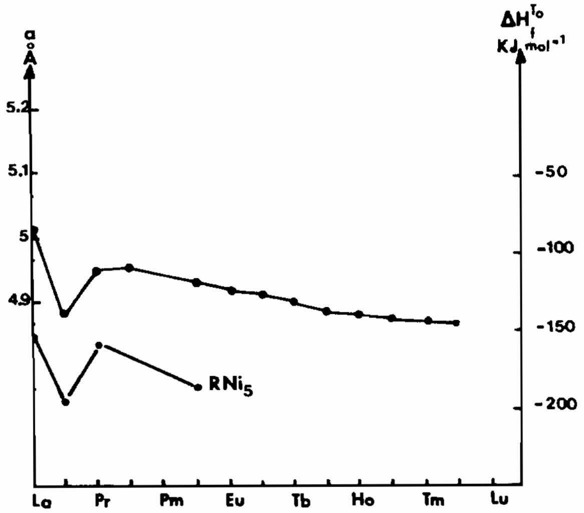

Fig. 1. *a* parameter and enthalpy of formation inside the lanthanide series.

Experimental enthalpies of formation are shown in Table I. Our value of the enthalpy of formation of $LaNi_5$ compound is in agreement with the more recent experimental values obtained by O'Hare [5] and S. Watanabe [6] which are −164 and −157.7 kJ mol^{-1} respectively.

The a lattice parameter and the variations of enthalpy of formation inside the series RNi_5 are presented in Fig. 1. The evolution of these two quantities is appreciably identical, the abnormal behaviour of Ce in $CeNi_5$ compound being exhibited in the two cases.

The variation of the enthalpy of formation can be explained by physical properties of the rare earth metals. Geschneidner [7] has explained the crystal structure sequence of the lanthanide metals when compressed or alloyed by the participation of the 4f electrons in the bonding for the light lanthanide metals (La to Ho). The 4f contribution to the bonding is essentially zero for the heavy lanthanide metals (Er to Lu). Geschneidner [8] found that the metallic radius of the rare earth r_R divided by the 4f orbital radius r_{4f}, calculated by Freeman [9], gives

TABLE I. Experimental and Calculated Values of the Enthalpies of RNi_5 Compounds.

Compound	ΔH_f^{298} experimental kJ mol^{-1}	r_R/r_{4f}	ΔH_f^{298} calculated kJ mol^{-1}
$LaNi_5$	−158.9	3	−150.6
$CeNi_5$	−199		
$PrNi_5$	−160.6	3.31	−165.2
$SmNi_5$	−182	3.635	−182
YNi_5	−204.6		

a number which is at least a qualitative estimate of the relative participation of the 4f electrons in the bonding in these metals.

The assumption of this radius ratio can be applied to the intermetallic compound and in our case allows us to calculate empirically the enthalpies of formation of RNi_5 compounds. The values of the enthalpies of formation of RNi_5 compounds where R is a heavy lanthanide metal must be equal to the value of the enthalpy of formation of the YNi_5 compoud (–204.6 kJ mol^{-1}) since Yttrium without 4f electrons has a behaviour similar to the heavy lanthanide metals. For the RNi_5 compounds, where R is a light lanthanide metal, the enthalpies of formation are deduced from the enthalpy of $ErNi_5$ by the study of the r_R/r_{4f} ratio. The calculated values are compared with the experimental ones in Table I. There is a good agreement between calculated and experimental results. This approach allows us to give an explanation about the peculiar value of the enthalpy of formation of $CeNi_5$ compound. If Ce has a behaviour similar to La and Pr in the RNi_5 compound, the enthalpy of formation of the $CeNi_5$ compound should be obtained by linear interpolation from the values of the enthalpies of formation of $LaNi_5$ and $PrNi_5$ compounds; the obtained value should be equal to –160 kJ mol^{-1}, value plainly different of the experimental value –199 kJ mol^{-1}.

Moreover the experimental values of the enthalpies of formation of $CeNi_5$ and YNi_5 compounds are very close and let us think that the 4f electrons of Ce do not participate in the bonding in the $CeNi_5$ compound.

Our energetic study does not allow us to conclude in favour of a valence state close to 4^+ of Ce in $CeNi_5$ compound, nevertheless our results are not in disagreement with this assumption and show that Cerium has effectively an abnormal behaviour in the $CeNi_5$ compound.

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Uranyl Complexes with Potentially Pentadentate Ligands. Crystal Structure of $UO_2\{[o\text{-}C_6H_4CH{=}N(CH_2)_3]_2OP(C_6H_5)\}$ and $UO_2\{[o\text{-}OC_6H_5{-}C(CH_3){=}N(CH_2)_2]_2NH\}$

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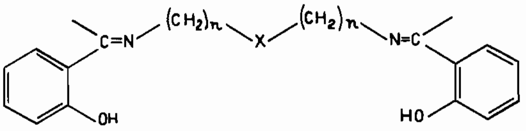
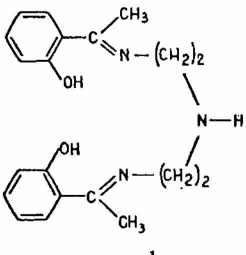
Uranyl(VI) complexes with Schiff bases have been extensively studied [1–3]; using, potentially bi-, ter-, tetra- and pentadentate ligands pentagonal bipyramidal coordination geometries are always obtained.

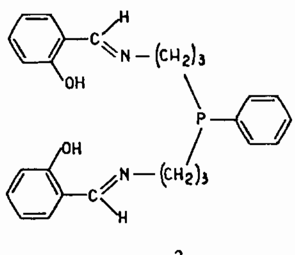
Recently we focused our interest in the preparation of a series of uranyl(VI) complexes with the pentadentate ligands of the type:



This paper deals with the preparation, the properties and the crystal structures of uranyl(VI) complexes with the ligands:



(H_2L^1)



(H_2L^2)

All the complexes can be easily prepared, as orange red powder, by reacting the performed Schiff bases with uranyl(VI) nitrate.

Crystals of $UO_2(L^1)$ are monoclinic, space group $P2_1/c$, $Z = 4$ with $a = 6.32(1)$, $b = 13.22(1)$, $c = 24.14(1)$ Å; $\beta = 92.61(2)°$. In this complex the ligand is pentadentate in the equatorial plane of the uranyl ion and the five coordinated atoms form a rather puckered pentagon.

Although the molecule has no imposed symmetry, the two wings of the ligands are approximately symmetrical forming dihedral angles of 37 and 40° with the coordination plane. They are also strongly inclined with each other with a dihedral angle of 71°.