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 UO2{[o-C6H4CH=N(CH2)3]2OP(C6H5)} and UO2{[o-OC6H5—C(CH3)=N(CH2)2]2NH}

U. CASELLATO, S. SITRAN, S. TAMBURINI, P. A. VIGATO*

*Istituto di Chimica e Tecnologia dei Radioelementi, CNR Padua, Italy*

and R. GRAZIANI

Istituto di Chimica Generale dell'Università, Padua, Italy

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:
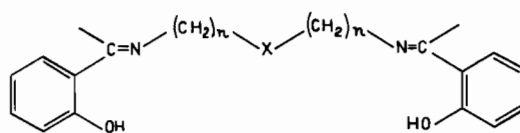

This paper deals with the preparation, the properties and the crystal structures of uranyl(VI) complexes with the ligands:
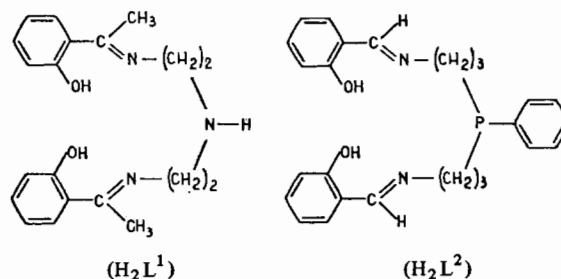
All the complexes can be easily prepared, as orange red powder, by reacting the performed Schiff bases with uranyl(VI) nitrate.

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; $\beta = 92.61(2)^\circ$. 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°.
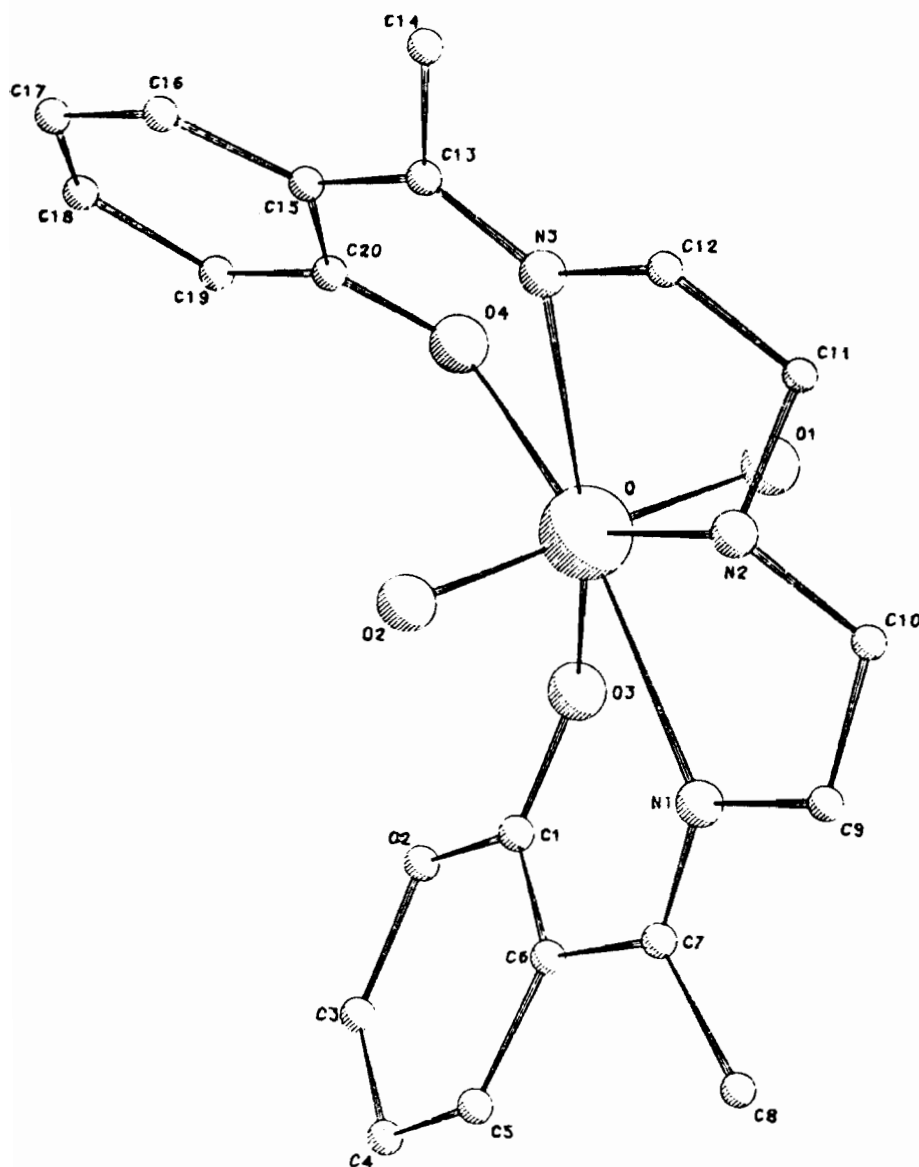
$UO_2(L^2)$ is stable in air and apparently does not change with time. The mass spectrum shows a very intense peak due to the parent P^+ ion at 699 m/e. During the recrystallization an oxidation of the phosphine group to phosphine oxide occurs; the new complex obtained $UO_2(L^{2'})$ has a different i.r. spectrum, especially in the $\nu P–O$ region, and is non-volatile also under drastic conditions.

Crystals of $UO_2(L^{2'})$ are orthorhombic, space group Pnma, $Z = 4$, with $a = 10.85(1)$, $b = 14.23(1)$, $c = 16.17(1)$ Å; the five donor atoms of the ligand are equatorially bonded to the uranyl group to form discrete, monomeric molecules with the seven coordinated metal in the usual distorted pentagonal bipy-

ramidal coordination geometry. The molecule lies across a crystallographic mirror plane which contains the uranyl group and the PhPO fragment. The five coordinated atoms form a puckered pentagon where the oxygen atoms are slightly displaced above and the nitrogen atoms below the equatorial mean plane. *(see next page)*

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