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A4

Organometallic Compounds of the Lanthanides with Ylide Ligands

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$LuCl_3$ reacts with $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yielding a 1:3 complex which shows dynamic behaviour in solution. The addition of $(C_5H_5)_2LuCl$ to $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yields an 1:1 chelate complex with stable configuration.

$(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ and $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ react with $CH_2{=}P(C_6H_5)_3$ and $Me_3SiCH{=}P(CH_3)_3$ in toluene with exchange of the THF ligand for the ylides and formation of new dicyclopentadienyl(alkyl)lutetinyl methylene triorganophosphoranes. New zwitterionic complexes of the type $(C_5H_5)_2Lu(R)(CHR'{=}PR''_3)$ have been isolated and characterized by their NMR spectra and by X-ray structural investigations.

Other ylide complexes of organolanthanides are unstable at room temperature. They decompose with evolution of hydrocarbons and formation of metallacycles or polymeric organolanthanide derivatives.

A5

New Aspects in the Chemistry of Uranocene

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A6

Lower Oxidation States of Lanthanides and Actinides

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A7

Recent Studies of Actinide Stereochemistry

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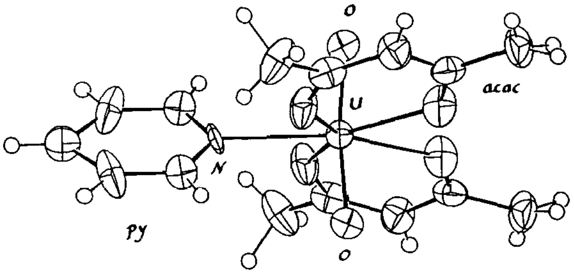
The result of recent work on co-ordination compounds will be described. Emphasis will be laid on the effects of changing the actinide element and on the detailed influence of the coordinating ligands. Among other examples, the structure of UO_2(pyridine)(acac)$_2$ will be discussed, which has been shown to contain a significantly bent O–U–O group (173.5(8)°); its crystals are orthorhombic, *Fdd2,* with a = 29.702(4), b = 11.433(2), c = 10.593(2), R(final) = 0.032:



A8

Electron Spin Resonance Study of Uranium(V) Intermediate in Both Processes of Photo- and Electrolytic Reductions of Uranyl Complex in Organic Solution

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Recently the appearance of pentavalent uranium was suggested indirectly by an analysis of photochemical- or electrolytic reduction processes of uranyl complexes in solution [1, 2] but we have first observed the electron spin resonance (ESR) spectra of uranium(V) and confirmed directly the existence of uranium(V) species on the way of both

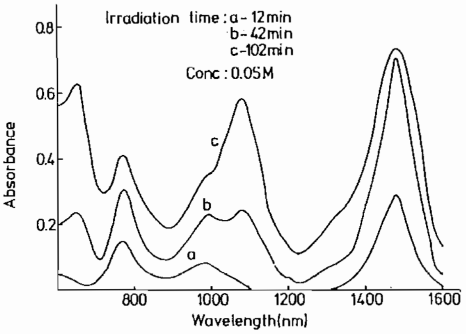

Fig. 1. Optical absorption spectra.

the photo- and electrolytic-reductions of uranyl complex in organic solution. The ESR spectra were nearly symmetric. This result is reasonably analyzed as the case of the g-factor with axial symmetry, $g_\perp = 2.5$ and $g_\parallel \sim 0$. Based on a crystalline field theory it is concluded that the uranium(V) species in question has the ligands more tightly in the equatorial plane rather than in the axial direction.

Pure $UO_2(DMF)_5(ClO_4)_2$ was synthesized according to the method described previously. Crystalline $UO_2(DMF)_5(ClO_4)_2$ was dissolved under nitrogen atmosphere in dimethylformamide (DMF) dried by molecular sieve before use, and the solution was degassed by freezing–pump–thaw cycles three or four times. For the photochemical reduction a 500 W high pressure mercury lamp was used as the light source. The reaction by electrolytic reduction was performed on a simple two-electrode cell specially designed for low temperature electron spin resonance measurements [3]. Optical absorption spectra were measured in the region of visible to near infrared. The ESR spectra were measured at liquid nitrogen temperature after irradiation at room temperature. The ESR spectra were very broad and almost symmetric. The intensity of spectra increases with increasing irradiation time at the beginning stage. After this solution was kept in the dark at room temperature for one week, the intensity became weaker than that before keeping the solution. When this solution was again irradiated the intensity got stronger like that before keeping. After keeping the solution for one further week, however, the spectra were no more observed and a dark suspension was remarked, which is likely an uranium hydroxide, while the color of the liquid part of the solution still remained yellow.

On the other hand, the optical spectra of the solution change with irradiation time with respect to the absorption peaks and intensities. As shown in Fig. 1 absorptions at 770, 990 and 1480 nm appeared as the beginning stage of irradiation. These peaks grew with further irradiation, accompanying simultaneously the appearance of absorption peaks at 660 and 1090 nm. Among these peaks three absorption peaks at 770, 990 and 1480 nm can be attributed to uranium(V) species and the remainders at 660 and 1090 nm to uranium(IV) species which originates from a disproportionation of the uranium(V) species.

The appearance of uranium(V) species on the way of photoreduction was further confirmed by the ESR measurement of this complex generated during the electrolytic reduction process. The applying voltage to the working electrode was determined to be −2.0 V by measuring the optical spectra in the course of electrolytic reduction. The ESR spectra obtained at −120 °C after electrolytic reduction were quite similar to those observed in photoreduction. The behavior of the ESR spectra in the electrolytic reduction time nicely corresponded to those in the case of photoreduction. The behavior of optical absorption did also to the case of photoreduction.

The values of $g_\perp$ estimated from the spectra is 2.5 in both reduction reactions and the line-widths are 1550 and 1250 gauss in the photo- and electrolytic reductions, respectively. These broad line-widths have often been observed by us about pentavalent uranium complexes or compounds in solid state [4]. The uranium(V) has a 5f electron and an isoelectronic configuration with neptunium(VI). It seems reasonably that uranium(V) produced by the reduction of the uranyl ion, UO_2^{2+}, has an analogous structure to the neptunyl ion, NpO_2^{2+}, where the axial field is predominant on neptunium(VI). Among Kramers doublets produced by splitting of $5f^1$ level under the crystal field with axial symmetry and spin–orbit coupling interaction, only $|\pm\frac{1}{2}\rangle$ has a definite value of both $g_\parallel$ and $g_\perp$; $g_\parallel = 2\sin^2\theta_1$ and $g_\perp = 2\sin^2\theta_1 + 4\sqrt{3}\sin\theta_1\cos\theta_1$. All others gave $g_\perp = 0$. In order to explain the experimental data, the ground state of $|\pm\frac{1}{2}\rangle$ is most reasonable. Such situation that $|\pm\frac{1}{2}\rangle$ is the ground state is probably the first case as far as we can be aware. These facts are supported by the ESR observation on NpO_2^{2+} doped in $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$ [5]. When we take ground state into account, the electronic spectra observed can also be reasonably explained.

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