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RIS(CYCLOPENTADIENYL)PLUTONIUM(IV) CHLORIDE AND HIOCYANATE, $(\eta^5\text{-}C_5H_5)_3PuCl$ AND $(\eta^5\text{-}C_5H_5)_3Pu(NCS)$

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ummary

The first cyclopentadienylplutonium(IV) compounds, $(\eta^5\text{-}C_5H_5)_3PuCl$ and $\eta^5\text{-}C_5H_5)_3Pu(NCS)$ have been prepared, the former by reaction of Cs_2PuCl_6 ith TlC_5H_5 in CH_3CN and the latter by treating the chloride with KNCS in trahydrofuran. Both compounds are isostructural with their U^{IV} and Np^{IV} nalogues. The IR and UV/visible spectra of the new compounds are reported.

ntroduction

Tris(cyclopentadienyl) plutonium(IV) compounds of the type $(\eta^5\text{-}C_5H_5)_3PuX$ ave not been recorded hitherto, although analogous compounds [1] have been nown for some time for thorium(IV), uranium(IV) and neptunium(IV), for hich tetrachlorides are available as starting materials. However, bis(cycloocta-traene)plutonium(IV), $Pu(C_8H_8)_2$, has been prepared [2] by adding solid $(C_2H_5)_4N\}_2PuCl_6$ to a THF solution of $K_2C_8H_8$, a reaction which failed with s_2PuCl_6, and also by reaction of C_8H_8 with finely divided plutonium metal [3]. he possibility of preparing cyclopentadienylplutonium(IV) compounds from exachloroplutonates(IV) was therefore investigated.

xperimental

All work was carried out in dry atmosphere, nitrogen-filled glove boxes vater $\lesssim$20 ppm, oxygen $\lesssim$20 ppm) to afford protection against the α-radiation nitted by ^{239}Pu and to protect the samples against atmospheric moisture.

The starting material, Cs_2PuCl_6, was prepared as previously described [4] ccept that precipitation was from cold, concentrated hydrochloric acid, and lC_5H_5 was prepared by the published method [5]. THF was dried by refluxing

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over $LiAlH_4$, and CH_3CN, CH_2Cl_2 and n-C_5H_{12} by refluxing over CaH_2; the dried solvents were then distilled under nitrogen. KNCS was vacuum dried (10^{-3} Torr/24 h).

Infrared spectra were recorded using a Perkin-Elmer 180 spectrometer, as Nujol mulls between CsI (4000—200 cm^{-1}) or silicon (300—180 cm^{-1}) plates. Electronic absorption spectra of solutions were recorded using a Cary 14 spectrophotometer (700—1600 nm) and X-ray powder diffraction photographs were obtained using a Debye-Scherrer 19 cm camera with Ni-filtered Cu-K_α radiation (λ = 1.5418 Å).

Preparative

Preliminary experiments showed that neither $\{(C_2H_5)_4N\}_2UCl_6$ nor Cs_2UCl_6 reacted with TlC_5H_5 in THF, but Cs_2UCl_6 reacted readily with TlC_5H_5 in CH_3CN. This last was therefore used as the preparative medium.

(η^5-C_5H_5)$_3$PuCl. Cs_2PuCl_6 (0.3851 g, 0.537 mmol) and TlC_5H_5 (0.4345 g, 1.612 mmol) were stirred together at room temperature in dry CH_3CN (ca. 5 ml). After 10 minutes the reaction mixture became chocolate brown; the mixture was stirred overnight (16 h), centrifuged and the very dark brown supernatant was evaporated to dryness in vacuo. The solid residue was washed with n-C_5H_{12} (2 × 1 ml), in which it was very slightly soluble, and then vacuum dried (2 h) to give a very dark brown powder (yield, 85%). (Found: Pu, 50.7; Cl, 7.3. $C_{15}H_{15}PuCl$ calcd.: Pu, 50.9; Cl, 7.6%).

(η^5-C_5H_5)$_3$PuNCS. (η^5-C_5H_5)$_3$PuCl (0.2079 g, 0.443 mmol) and KNCS (0.04289 g, 0.441 mmol) were stirred together (16 h) in dry THF (ca. 5 ml); after centrifugation, the very dark supernatant was vacuum evaporated to dryness, and the residue was extracted into CH_2Cl_2. The extract was evaporated to dryness and the residue washed with n-C_5H_{12} (2 × 1 ml), in which it was very slightly soluble, and then vacuum dried (2 h) to give a black solid (very dark brown when finely divided) (yield, 45%). (Found: Pu, 47.4; NCS, 11.9 $C_{16}H_{15}NSPu$, calcd.: Pu, 48.5; NCS, 11.8%).

Analyses

The complexes were dissolved in the minimum volume of acetone and 50% aqueous ammonia solution was added dropwise to precipitate plutonium(IV) hydroxide. The centrifuged precipitate was washed with water followed by aqueous acetone and the supernatants were collected together. The precipitate was ignited to constant weight (PuO_2). The analytical results for chloride [6] and thiocyanate [7] in the supernatants were obtained by published methods.

Results and discussion

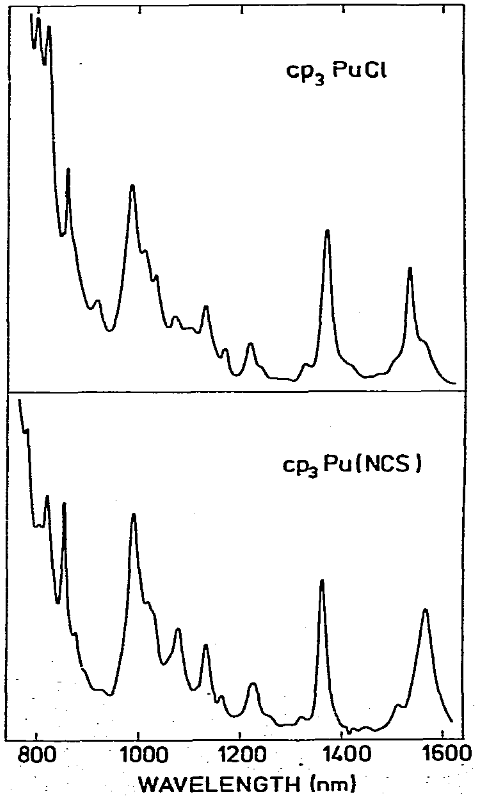
(η^5-C_5H_5)$_3$PuCl and (η^5-C_5H_5)$_3$PuNCS are very dark brown to black, moisture-sensitive solids and in solution are particularly susceptible to hydrolysis. Both compounds are completely soluble in THF and in CH_3CN, but are only very slightly soluble in n-C_5H_{12}. (η^5-C_5H_5)$_3$PuCl does not sublime in vacuo (10^{-3} Torr) at 140—230°C, but a slight colour change is observed above 140°C. The infrared spectra of the two compounds are very similar to those of the analogous uranium and neptunium complexes (Table 1).

ABLE 1

NFRARED SPECTRA (cm^{-1}) OF (η^5-C_5H_5)$_3$PuCl AND (η^5-C_5H_5)$_3$PuNCS (data for U^{IV} and Np^{IV} hown in parentheses)

$\eta^5C_5H_5)_3PuCl$	$(\eta^5 C_5H_5)_3Pu(NCS)$
095w, ν(CH)	3085w, ν(CH)
	2035vs, ν(CN)
	1725w
155w	1120w
055w	1062w
015sh 006m } δ(CH)	1018sh 1008m } δ(CH)
	971w
	959vw
924w	910w
	830m, ν(CS)
784s, π(CH)	795s, π(CH)
263m, ν(Pu—Cp) [a] J, 266; Np, 266)	248m, ν(Pu—Cp) (U, 246; Np, 246)
230m, ν(Pu—Cl) [a] J, 241; Np, 234)	

Tentative assignments; Pu—Cp represents the metal-ring mode and it is uncertain which features refer this and the Pu—Cl mode (e.g. see ref. 8).



g. 1. The UV/visible spectra of (η^5-C_5H_5)$_3$PuCl and (η^5-C_5H_5)$_3$PuNCS (700—1600 nm) in THF solution.

The most striking feature of the UV visible spectra of $(\eta^5\text{-}C_5H_5)_3PuCl$ and $(\eta^5\text{-}C_5H_5)_3Pu(NCS)$, shown in Fig. 1 is the extension of an intense charge transfer band almost up to 800 nm; the spectra of the two compounds are very similar in all respects, suggesting that the environment of the plutonium is the same in the two compounds. X-ray powder diffraction photographs also show that the two plutonium compounds are isostructural with their uranium(IV) and neptunium(IV) analogues.

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