Preparation and Properties of Trichlorobis(pentane-2,4-dionato)protactinium(V), Tetrakis(1,3-diphenylpropane-1,3-dionato)protactinium(IV), and Tetrakis(pentane-2,4-dionato)actinoid(IV) Complexes

By **David Brown,* Brian Whittaker, and John Tacon**, Chemistry Division, Building 220, A.E.R.E., Harwell

Trichlorobis(pentane-2,4-dionato)protactinium(V), $[PaCl_3(pd)_2]$, has been obtained from the reaction between protactinium pentachloride and pentane-2,4-dione (Hpd) in methylene dichloride, and $[Pa(dppd)_4]$ and $[Pa(dp)_4]$ (dppd = 1,3-diphenylpropane-1,3-dionato) from reactions involving the thallium salt of the appropriate chelate and $[Et_4N]_2[PaCl_6]$ and $PaCl_4$, respectively, in oxygen-free non-aqueous solvents. Oxidation of $[Pu(pd)_3]$ in solvents such as benzene and ethanol in the presence of Hpd yields $[Pu(pd)_4]$. Attempts to prepare $[Am(pd)_4]$ and complexes of the type $M[Th(pd)_5]$ (M = univalent cation) have been unsuccessful. *X*-Ray diffraction results are reported for the above complexes, together with details of conditions necessary for formation of the α and β phases of the tetrakis(pentane-2,4-dionato)actinoid(IV) complexes. Solid-state spectral results (0·5—2·2 μm) are provided for β-$[Pa(pd)_4]$, β-$[U(pd)_4]$, β-$[Pu(pd)_4]$, and $[Pu(pd)_3]$ together with i.r. results for these complexes, those of the type $[M(pd)_4]$ (M = Zr, Hf, Ce, and Th), and $[PaCl_3(pd)_2]$.

COMPLEXES of protactinium with organic chelates have barely been investigated. Thus, information is available only for the quinquevalent tropolonates [1,2] $[Pa(tpl)_4X]$ (tpl = tropolonato; X = Cl, Br, ClO_4, or OEt) and $[Pa(tpl)_4Cl]$,dmso (dmso = dimethyl sulphoxide), the quinquevalent *N,N*-diethyldithiocarbamates [3] $[Pa(detc)_4X]$ (detc = *N,N*-diethyldithiocarbamate; X = Cl or Br), and quadrivalent complexes of the types $[PaL_4]$ (L = tpl [2] or η-cyclopentadiene [4]), $M[Pa(tpl)_5]$ [2] and $[PaL_2]$ (L = phthalocyanine [5,6] or η-cyclo-octatetraene [7]).

Stable pentane-2,4-dionate complexes of the type $[M(pd)_4]$ are known [8] for several of the earlier members of the actinoid series (M = Th, U, Np, or Pu) but $[Pa(pd)_4]$ has not previously been characterised. In addition, complexes of the type $M'[M(pd)_5]$ (M' = univalent cation, M = actinoid element) and $[M(pd)_xCl_{5-x}]$ (M = actinoid, x = 0—5 inclusive) appear to be unknown. It was therefore of interest to investigate the preparation of $[Pa(pd)_4]$, and the related $[Pa(dppd)_4]$ (dppd = 1,3-diphenylpropane-1,3-dionato), particularly in view of the apparent instability [9] of $[Pa(detc)_4]$ relative to the analogous complexes formed by Th, U, Np, and Pu, and to explore the possibility of obtaining complexes of the type $M'[M(pd)_5]$ and actinoid(V) pentane-2,4-dionates. During the course of these investigations tris(pentane-2,4-dionato)plutonium(III) was prepared for the first time and oxidised to tetrakis(pentane-2,4-dionato)plutonium(IV) by oxygen in the presence of an excess of pentane-2,4-dione (Hpd) (*cf.* the analogous Ce^{III} oxidation [10]), and the preparation of $[Am(pd)_4]$ by a similar reaction was also attempted.

Although both α and β modifications have been reported for some complexes of the type $[M(pd)_4]$ (M = Ce, Th, and U), conditions for their reproducible preparation appear not to have been established. We therefore investigated the conditions under which the different crystal modifications of these actinoid complexes (M = Th, Pa, U, and Pu) are obtained. In addition, unit-cell dimensions have been derived for the complexes $[Pa(pd)_2Cl_3]$, β-$[Pa(pd)_4]$, and β-$[Pu(pd)_4]$, solid-state transmission spectra have been recorded for the last two complexes, for α- and β-$[U(pd)_4]$ and for $[Pu(pd)_3]$, and i.r. spectra (4 000—50 cm^{-1}) of all these complexes and other tetrakis(pentane-2,4-dionato)metallates(IV) (M = Ce, Th, Zr, and Hf) have been studied.

RESULTS AND DISCUSSION

Some Chemical and X-Ray Diffraction Properties of the Actinoid Pentane-2,4-dionates and Tetrakis(1,3-diphenylpropane-1,3-dionato)protactinium(IV).— Protactinium pentachloride reacted rapidly and exothermically with an excess of Hpd in anhydrous methylene dichloride to yield a bright yellow solution from which trichlorobis(pentane-2,4-dionato)protactinium(V), $[PaCl_3(pd)_2]$, was obtained as yellow needle crystals on addition of anhydrous isopentane. This moisture-sensitive complex undergoes rapid hydrolysis on the addition of aqueous ammonia; it is soluble in methylene dichloride, methyl cyanide, methanol, and ethanol. Similar reactions involving uranium pentachloride and an excess of Hpd yielded only tetrakis(pentane-2,4-dionato)uranium(IV), the same product also being obtained from reactions between uranium pentachloride and Tl(pd) (1 : 5 and 1 : 4 mol ratios of reactants) in methylene dichloride. The latter reactions are also exothermic. With smaller amounts of Tl(pd) [reactions involving 1 : 1, 1 : 2, and 1 : 3 mol ratios of UCl_5 and Tl(pd)] we obtained evidence from *X*-ray powder-diffraction analysis for the existence of trichlorobis(pentane-2,4-dionato)uranium(V), $[UCl_3(pd)_2]$, which is isostructural with the protactinium(V) analogue, and two other products, one of which, from analytical

---

[1] D. Brown and C. E. F. Rickard, Tagungsbericht der 3rd Internat. Protaktiniumkonferenz, Schloss Elmau, April 1969, BMBW-F3 K 71-17, 1971, paper 21.1.

[2] D. Brown and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 3373.

[3] P. R. Heckley, D. G. Holah, and D. Brown, *Canad. J. Chem.*, 1971, **49**, 1151.

[4] F. Baumgärtner, E. O. Fischer, B. Kannellakopolus, and P. Laubereau, *Angew. Chem.*, 1969, **81**, 182.

[5] D. Brown, R. D. Fischer, F. Lux, D. Dempf, and W. Hagenberg, ref. 1, paper 23.1.

[6] F. Lux, D. Brown, D. Dempf, R. D. Fischer, and W. Hagenberg, *Angew. Chem. Internat. Edn.*, 1969, **8**, 894.

[7] J. Goffart, J. Fuger, D. Brown, and G. Duyckaerts, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 413; D. F. Starks, T. C. Parsons, A. Streitweiser, jun., and N. Edelstein, *Inorg. Chem.*, 1974, in the press.

[8] K. W. Bagnall in 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon, London, 1973, vol. 5, p. 417.

[9] K. W. Bagnall, D. Brown, and D. G. Holah, *J. Chem. Soc.* (*A*), 1968, 1149.

[10] T. J. Pinnavaia and R. C. Fay, *Inorg. Synth.*, 1970, **12**, 77.

results, appears to be $[UCl_2(pd)_3]$. These reactions were not studied in detail; however, it does appear that the composition of the major product in a given reaction is not dependent only on the ratio of the reactants, and exact conditions for the preparation of pure $[UCl_3(pd)_2]$ and $[UCl_2(pd)_3]$ were not established.

The reaction between protactinium tetrachloride and Tl(pd) (1 : 4 mol ratio) took place only slowly in benzene due to the low solubilities of the reactants. However, it proceeded rapidly in oxygen-free ethanol and vacuum evaporation of the resulting blue solution, followed by recrystallisation of the product from hot cyclohexane, yielded dark violet β-[Pa(pd)$_4$], which is also soluble in benzene, methylene dichloride, and methyl cyanide. The β modifications of [U(pd)$_4$] and [Pu(pd)$_4$] were also consistently obtained on recrystallisation from hot cyclohexane, but we were unable to obtain pure β-[Th(pd)$_4$] by this procedure. This is apparently due to the speed of the $\beta \longrightarrow \alpha$ transformation at room temperature, since *X*-ray powder photographs recorded immediately following recrystallisation showed the product to be a mixture of α- and β-[Th(pd)$_4$] whilst films recorded 24 h later showed the transformation to α-[Th(pd)$_4$] to be complete. A similar mixture of phases was obtained initially on crystallisation from hot benzene followed by heating the product in air at 105 °C. These observations suggest that this $\beta \longrightarrow \alpha$ transformation occurs more rapidly than reported[11] by Gredenić and Matković.

The β modifications of the actinoid(IV) pentane-2,4-dionates increase in stability relative to the α phases with decreasing ionic radius of the actinoid(IV) ion {thus only β-[Pu(pd)$_4$] exists} and, in view of the fact[12] that $[Et_4N]_2[ThCl_6]$ containing 5% of the slightly smaller Pa^{IV} ion crystallises from methyl cyanide in the β modification (as do the pure complexes for the elements Pa to Pu inclusive) whereas pure $[Et_4N]_2[ThCl_6]$ is invariably obtained as the α modification under these conditions, we attempted to stabilise β-[Th(pd)$_4$] by introducing Zr into the lattice. Despite the fact that [Zr(pd)$_4$] is known only as the β modification, crystallisation of [Th(pd)$_4$] containing 5% Zr^{IV} failed to stabilise β-[Th(pd)$_4$]. Similar results were obtained with 5% U^{IV} in [Th(pd)$_4$].

The phase α-[U(pd)$_4$] was reproducibly obtained by cold, vacuum, evaporation of solutions of the β modification in non-aqueous solvents such as benzene, ethanol, and cyclohexane. However, despite this, and the stability of α-[Th(pd)$_4$], we were unable to prepare α-[Pa(pd)$_4$] by similar methods, including crystallisation from isopentane at *ca.* 100 °C. This appears to be due to the small amounts of [Pa(pd)$_4$] used (5—15 mg), since with similar small quantities of the uranium(IV) analogue we also obtained the β modification under these conditions {amounts in excess of 50 mg resulting in formation of α-[U(pd)$_4$]}. Attempts to convert β- to α-[Pa(pd)$_4$] by cooling the solid in liquid nitrogen were also unsuccessful, and no phase change occurred when the β phase was kept in a sealed *X*-ray capillary for 7 weeks at room temperature.

Tris(pentane-2,4-dionato)plutonium(III) was obtained from aqueous solution using the method reported[10] for [Ce(pd)$_3$]. Recrystallisation from benzene yielded dark green crystals which were isostructural with [Nd(pd)$_3$]. When dissolved in non-aqueous solvents, such as benzene and ethanol, containing an excess of Hpd, it was oxidised quantitatively to tetrakis(pentane-2,4-dionato)-plutonium(IV) by oxygen. The resulting orange-brown product is appreciably soluble in such solvents, from which it crystallises as the β modification (quantities ranging from 5 to 75 mg) on cold, vacuum, evaporation of the solvent {*cf.* α-[Th(pd)$_4$] and α-[U(pd)$_4$] by this method}. We observed no evidence for the formation of α-[Pu(pd)$_4$]. Since very few simple americium(IV) complexes are known, we attempted to convert [Am(pd)$_3$] into [Am(pd)$_4$] by this method. However, although a slow colour change, yellow $\longrightarrow$ red, did occur when oxygen was bubbled through non-aqueous solvents (benzene and alcohol) containing [Am(pd)$_3$] precipitated from aqueous media or prepared in alcohol, this was reversed when the oxygen was removed during vacuum evaporation of the solvent and when the solution was allowed to stand in a nitrogen-atmosphere box. The products from various experiments involving ^{241}Am (10—20 mg) were all amorphous and we were unable to identify them with certainty. Although the americium content of samples isolated rapidly was close to that of [Am(pd)$_4$], the product failed to redissolve in benzene or alcohol, behaviour contrasting with that of the actinoid(IV) analogues. Similar attempts to obtain [Am(dppd)$_4$] were also unsuccessful, although similar colour changes were observed. In view of the intense radiation associated with ^{241}Am, it may prove profitable to study these reactions using the longer-lived isotope, ^{243}Am.

Attempts to prepare pentakis(pentane-2,4-dionato) complexes of thorium(IV) and uranium(IV), *e.g.* M′[M(pd)$_5$] (M′ = univalent cation, M = Th or U) by reactions between the appropriate tetrakis(pentane-2,4-dionate) and thallium or lithium pentane-2,4-dionate, thorium tetrachloride and Li(pd) in the presence of tetraethylammonium chloride (1 : 5 : 1 mol ratio of reactants), and thorium tetrachloride, piperidine, and Hpd in ethanol were also unsuccessful. The product in all instances was the appropriate tetrakis(pentane-2,4-dionate).

Tetrakis(1,3-diphenylpropane-1,3-dionato)protactinium(IV), [Pa(dppd)$_4$], was formed by the reaction between $[Et_4N]_2[PaCl_6]$ and Tl(dppd) in oxygen-free anhydrous methylene dichloride. Vacuum evaporation of the resulting green solution, followed by extraction of the crude product into benzene and vacuum evaporation of this solvent, yielded dark green, crystalline, [Pa(dppd)$_4$]. It is an air-sensitive solid which undergoes simultaneous oxidation and hydrolysis on addition of aqueous ammonia containing oxygen.

---

[11] D. Gredenić and B. Matković, *Acta Cryst.*, 1959, **12**, 817.

[12] D. Brown and B. Whittaker, unpublished work.

Single-crystal Weissenberg studies showed $[PaCl_3(pd)_2]$ to possess monoclinic symmetry, space group C_{2h}^{5} $(P2_1/c)$ with the unit-cell dimensions shown in Table 1. The calculated density for $Z = 8$ is $2{\cdot}058$ g cm^{-3}. *X*-Ray powder-diffraction results for β-$[Pa(pd)_4]$ were indexed on the basis of the data available[13] for β-$[U(pd)_4]$. The unit-cell dimensions for β-$[Pu(pd)_4]$ were obtained by single-crystal Weissenberg and precession studies. Results for both complexes are compared with those available for isostructural tetrakis (pentane-2,4-dionates) in Table 1. All dimensions refer to the space group C_{2h}^{6} $(C2/c)$ employed by Titze[13,14] rather than the related space group C_{2h}^{6} (I_2/c) used by Gredenić and Matković[11] [but erroneously quoted as C_{2h}^{6} $(C2/c)$ by these authors]. The values shown for β-$[Th(pd)_4]$ were converted from those quoted for space group $C_{\ h}$ $(I2/c)$; these values and the related unit-cell volume suggest that the original ones are in error since they should be larger than the corresponding values for the β modifications of the other actinoid complexes. The complex $[Pa(dppd)_4]$ is isostructural with $[U(dppd)_4]$; although adequate to permit identification, the *X*-ray powder-diffraction films of $[Pa(dppd)_4]$ were not good enough to allow calculation of reliable lattice parameters for the very large unit cell {*cf.* $[U(dppd)_4]$ is orthorhombic,[15] with $a_0 = 10{\cdot}303$, $b_0 = 20{\cdot}136$, and $c_0 = 23{\cdot}613$ Å in space group D_{2h}^{10} $(Pccn)$}.

TABLE 1

Lattice parameters for $[Pa(pd)_2Cl_3]$ and actinoid(IV) pentane-2,4-dionates

		Lattice parameters [a]				
Complex	Colour	a_0/Å	b_0/Å	c_0/Å	β/°	V/Å^3
$[PaCl_3(pd)_2]$ [b]	Yellow	8·01	23·24	18·63	98·9	3456
β-$[Th(pd)_4]$ [c]	White	21·90	8·38	14·37	115·78	2375
β-$[Pa(pd)_4]$ [b]	Blue	22·06	8·42	14·51	115·75	2427
β-$[U(pd)_4]$ [d]	Brown	22·021	8·390	14·486	115·72	2411
β$[Np(pd)_4]$ [e]	Green	22·06	8·38	14·42	116·23	2391
β$[Pu(pd)_4]$ [b]	Brown	21·70	8·46	14·36	115·14	2387
β$[Ce(pd)_4]$ [d]	Brown	22·006	8·378	14·371	115·78	2386
β-$[Zr(pd)_4]$ [d]	White	21·671	8·363	14·118	116·67	2286

[a] All β-$[M(pd)_4]$ complexes possess space group C_{2h}^{6} $(C2/c)$; $[PaCl_3(pd)_2]$ crystallises in space group C_{2h}^{5} $(P2_1/c)$. [b] This work. [c] Ref. 11, values converted from space group $I2/a$ into $C2/c$. [d] Ref. 13. [e] Ref. 14.

Visible and Near-i.r. Spectra.—Spectral data (in the range 0·8—2·0 μm) have recently been published[16,17] for a series of hexahalogenoprotactinates(IV) together with an assignment of the electronic transitions and calculated values for the ligand-field and spin–orbit-coupling parameters. The solid-state spectrum of eight-co-ordinate β-$[Pa(pd)_4]$ (Figure 1) was, as would be expected, quite different from those of the octahedral hexahalogenoprotactinates(IV). Assignment of electronic transitions for other than octahedral $5f^1$ complexes is extremely difficult and we prefer at this stage to merely report the spectrum, which undoubtedly will contain vibronic bands in addition to those due to pure electronic transitions. It is worth noting, however, that the spectrum is quite different from that of $[Et_4N]_4[Pa(NCS)_8]$[18] in which the Pa^{IV} atom exhibits cubic stereochemistry, but comparison with solid-state spectra available[19] for other eight-co-ordinate square-antiprismatic protactinium(IV) complexes and for dodecahedral protactinium(IV) complexes indicates that the spectral results cannot be used to distinguish these latter stereochemistries. Similar comments apply to the spectrum of β-$[U(pd)_4]$ shown in Figure 2. This spectrum is virtually identical with that of α-$[U(pd)_4]$, which also exhibits slightly distorted square-antiprismatic stereochemistry,[20] and with spectra of the complex in non-aqueous solvents such as benzene, indicating that there is no change of stereochemistry on

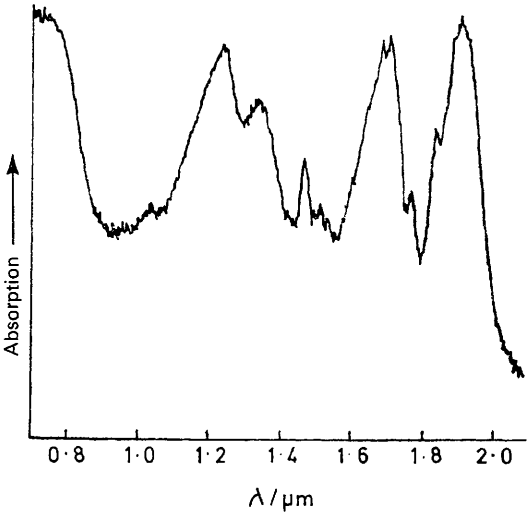

FIGURE 1 Solid-state spectrum of β-$[Pa(pd)_4]$ at 85 K

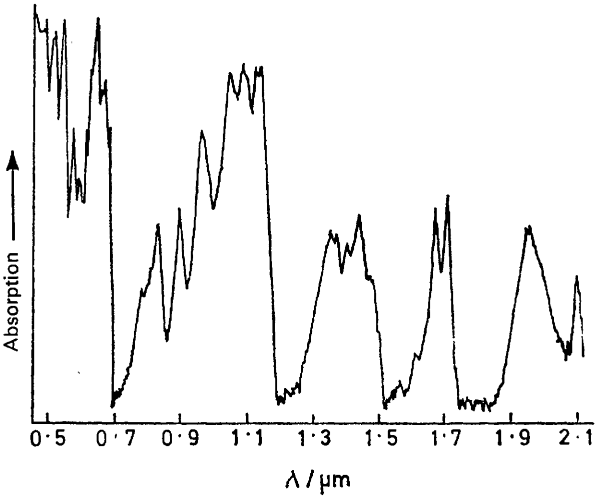

FIGURE 2 Solid-state spectrum of β-$[U(pd)_4]$ at 85 K

---

[13] H. Titze, *Acta Chem. Scand.*, 1970, **24**, 405.

[14] H. Titze, *Acta Chem. Scand.*, 1970, **24**, 715.

[15] V. L. Wolf and H. Bärnhighausen, *Acta Cryst.*, 1960, **13**, 778.

[16] N. Edelstein, D. Brown, and B. Whittaker, *Inorg. Chem.*, 1974, **13**, 563.

[17] D. Brown, B. Whittaker, and N. Edelstein, *Inorg. Chem.*, 1974, **13**, 1805.

[18] Z. M. S. Al-Kazzaz, K. W. Bagnall, D. Brown, and B. Whittaker, *J.C.S. Dalton*, 1972, 2273.

[19] D. Brown, B. Whittaker, and N. Edelstein, Brit. Report AERE-R 7481, 1972.

[20] D. Gredenić and B. Matković, *Nature*, 1958, **182**, 465; *Acta Cryst.*, 1959, **12**, 817.

dissolution in such solvents. This behaviour contrasts with that of $[Et_4N]_4[U(NCS)_8]$, for which, on the basis of structural data for this salt [21] and for $Cs_4[U(NCS)_8]$ [22] and spectral data for both salts,[18] the stereochemistry changes from cubic to square antiprismatic on dissolution in non-aqueous solvents. The solid-state spectra of $[Pu(pd)_3]$ and β-$[Pu(pd)_4]$ are illustrated in Figures 3(*a*) and (*b*), respectively; the latter may be compared with the spectrum of $[Pu(detc)_4]$ in benzene.[9]

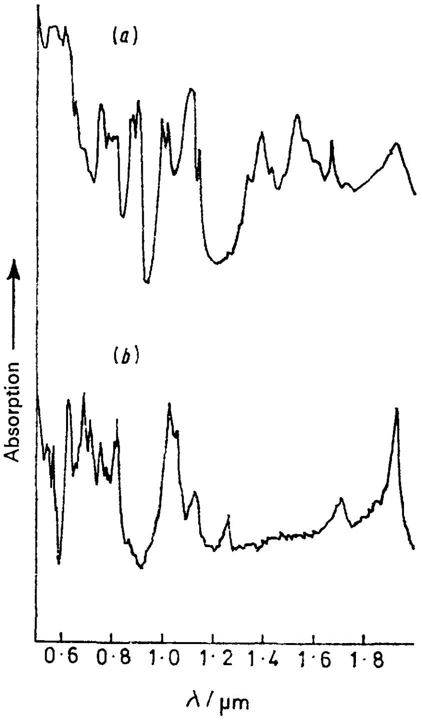

FIGURE 3 Solid-state spectra at 85 K of (*a*) $[Pu(pd)_3]$ (*b*) β-$[Pu(pd)_4]$

I.r. Spectra.—The i.r. spectra of the tetrakis(pentane-2,4-dionates) examined during this investigation were very similar in the region 1 600—700 cm^{-1} to those reported and interpreted previously [23-26] for a variety of bis- and tris-(pentane-2,4-dionates); bands observed in this region for benzene solutions of certain tetrakis-(pentane-2,4-dionates) (M = Zr, Hf, Ce, and Th) have been assigned previously [27] and will not be listed again. The major differences between these solution spectra and our spectra of the solids as Nujol mulls occurred in the 750—800 cm^{-1} region where the single band observed at *ca.* 770 cm^{-1} (C–H out-of-plane bending mode) for solution spectra was split into two or three bands, suggesting that the C–H protons in the solid occupy non-equivalent sites.

The bands we recorded below 700 cm^{-1} for the actinoid tetrakis(pentane-2,4-dionates) (M = Th, Pa, and U) are compared in Table 2 with results for β-$[Zr(pd)_4]$, β-$[Hf(pd)_4]$, α-$[Ce(pd)_4]$, and β-$[Ce(pd)_4]$. In general, the positions were close to those reported [27] for benzene solutions of certain of these complexes but more details of shoulders and weak–medium intensity bands below 170 cm^{-1} were present. The band at *ca.* 650 cm^{-1} also occurred in the spectrum of $[PaCl_3(pd)_2]$ and has been observed [23-26] in spectra of a variety of complexes of the types $[M(pd)_2]$ (M = bivalent *d* transition element) and $[M(pd)_3]$ (M = Fe and lanthanoid elements). In addition, bands were observed in the spectra of these bis- and tris-(pentane-2,4-dionates) in the region 420—480 cm^{-1}. Apart from these similarities, the spectra of the tetrakis(pentane-2,4-dionates) were quite different from those of such complexes in the region 700—50 cm^{-1}. In the absence of a co-ordinate analysis for 1 : 4 pentane-2,4-dionates, one can only confidently assign the most metal-sensitive strong bands and associated shoulders (Table 2 and Figure 4) to M–O stretching vibrations. On the basis of previous assignments, based on a co-ordinate analysis for a 1 : 1 complex,[23,25,26] for tris- and bis-(pentane-2,4-dionates), Fay and Pinnavaia [27] reported that the band [(I) in

TABLE 2

I.r. bands [a,b] (700—50 cm^{-1}) for the tetrakis(pentane-2,4-dionates)

Band no.	β-$[Zr(pd)_4]$	β-$[Hf(pd)_4]$	α-$[Ce(pd)_4]$	β-$[Ce(pd)_4]$	α-$[Th(pd)_4]$	β-$[Pa(pd)_4]$	α-$[U(pd)_4]$	β-$[U(pd)_4]$	β-$[Pu(pd)_4]$
(I)	659m	659m	656m	655m	655m	650m	655m	655m	655m
(II)	563w	563w	556w	557w	561w	559w	559w	557w	557w
(III)	537m	539m	523m	523m	521m	520m	523m	521m	521m
	530m	531m							
(IV) [c]	422s	425s	400s	400s	400s	402s	398s	400s	404s
	416s	418(sh)							
(V) [c]	310(sh)	267(sh)							
(VI) [c]	295s	245s	250s	250s	220s	216s	220s	220s	222s
(VII) [c]	274(sh)	230(sh)	236(sh)	236(sh)					
(VIII) [c]	240w		208w (sh)						
(IX)	190w	200(sh)	192w (sh)	192w (sh)	192(sh)	194(sh)	196(sh)	192(sh)	196(sh)
(X)			152w	146w	154m	140(sh)	162(sh)	144w	145w

[a] s = Strong, m = medium, w = weak, and sh = shoulder. [b] The reason for numbering the bands as shown is apparent from comparison of the spectra of β-$[Zr(pd)_4]$, α-$[Ce(pd)_4]$, α-$[U(pd)_4]$, and β-$[U(pd)_4]$ shown in Figure 4. [c] Probably predominantly M–O (asym.) stretching vibrations.

---

[21] R. Countryman and W. S. McDonald, *J. Inorg. Nuclear Chem.*, 1971, **31**, 2213.

[22] D. Brown, P. T. Moseley, and G. Bombieri, unpublished work.

[23] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, 1960, **32**, 588.

[24] M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, 1967, **A23**, 1037.

[25] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 1967, **6**, 433.

[26] S. Misumi and H. Iwasaki, *Bull. Chem. Soc. Japan*, 1967, **40**, 550.

[27] R. C. Fay and T. J. Pinnavaia, *Inorg. Chem.*, 1968, **7**, 508.

Table 2] at *ca.* 655 cm^{-1} in tetrakis(pentane-2,4-dionates) also has a contribution from a M–O stretching vibration. However, a full co-ordinate analysis for 1 : 3 complexes indicated [24] that this band is due only to ligand vibrations and, in view of the relatively slight shifts which occur both with change in stoicheiometry and stereochemistry and with the mass of the heavy atom for the various 1 : 2, 1 : 3, and 1 : 4 pentane-2,4-dionates, and considering also that two extra bands [Table 2, (II) and (III)] are present in the spectra of the last class of complex relative to those of the first two classes, the assignment of this band to a M–O stretching vibration cannot be viewed with confidence. Strong bands in the 420—480 cm^{-1} range have been shown [23-26] to be due predominantly to contributions from M–O stretching vibrations in 1 : 2 and 1 : 3 complexes and the metal-sensitive nature of this band [Table 2, (IV)] suggests that possibly this may also be true for the tetrakis-(pentane-2,4-dionates). However, it should be noted that we also observed a strong band at 400 cm^{-1} in the spectra of complexes of the type [M(pd)$_3$] (M = Nd, Ce, and Pu) with medium-intensity bands at 420 and 393 cm^{-1}.

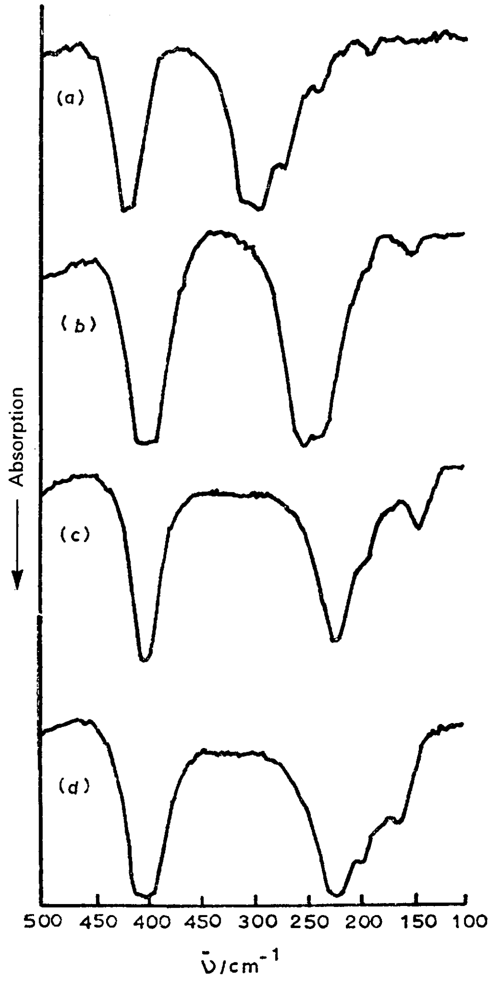

FIGURE 4 I.r. spectra of (*a*) β-[Zr(pd)$_4$], (*b*) α-[Ce(pd)$_4$], (*c*) α-[U(pd)$_4$], and (*d*) β-[U(pd)$_4$]

The shifts in position of the most metal-sensitive band [Table 2, (VI)] correlate better with the relative masses of the central metal atoms than with their ionic radii (or relative charge densities). However, that between Ce and Hf (*ca.* 4 cm^{-1}) is small relative to the others and the related mass differences, suggesting that effects due to electronic configuration (Zr^{IV} and Hf^{IV}, d^0; Ce^{IV}, $d^{10}f^0$), such as π-bonding to the *d* orbitals, are important.

The only significant difference between the spectra of the α and β modifications of [Ce(pd)$_4$] and [U(pd)$_4$] is associated with band (X) (Table 2), which, as shown in Figure 4, occurred at lower frequency and with increased intensity for the β modifications. No bands were observed in this region of the spectra for β-[Zr(pd)$_4$] and β-[Hf(pd)$_4$], but a medium-intensity band did occur in the spectra of the trivalent complexes [M(pd)$_3$] (M = Ce, Nd, and Pu) at *ca.* 150 cm^{-1}.

In addition to bands at 647, 543, 509, and 416 cm^{-1} (*cf.* Table 2), the spectrum of [PaCl$_3$(pd)$_2$] contained a strong band at 307 cm^{-1} and a broad feature at 290 cm^{-1} with an associated shoulder at 270 cm^{-1}. These last three bands are probably associated with Pa–Cl {*cf.* Cs[PaCl$_6$] [28] and [Et$_4$N]$_2$[Pa(O)Cl$_5$] [29] have bands at 305 cm^{-1}, and at 251 and 289 cm^{-1}, respectively} and/or Pa–O stretching vibrations. Strong broad bands at 210 cm^{-1} in the spectra of [Pa(dppd)$_4$] and [U(dppd)$_4$] are probably associated with M–O stretching vibrations; other weak–medium intensity bands occurred at 605, 515, 431, 249, and 164 cm^{-1} in the spectrum of the latter complex.

EXPERIMENTAL

Reagents.—All work with ^{231}Pa, ^{239}Pu, and ^{241}Am was carried out in glove-boxes because of the radioactivity associated with these isotopes. Inert-atmosphere boxes were utilised where necessary (oxygen <20 p.p.m.; water <20 p.p.m.), for example, for the preparation and manipulation of the readily oxidised protactinium(IV) complexes and the readily hydrolysed protactinium(V) and uranium(V) complexes. Protactinium and uranium pentachloride,[30] thorium,[31] protactinium,[32] and uranium tetrachloride,[33] and tetrakis(pentane-2,4-dionato)cerium(IV) [10] were prepared according to the references cited; [U(dppd)$_4$] was obtained from the reaction between UCl$_4$ and Tl(dppd) in ethanol. The halides were purified by vacuum sublimation prior to use. Commercial hafnium and zirconium tetrachloride were sublimed before use. Zirconium dichloride oxide hydrate (B.D.M. Ltd.) and cerium(III) nitrate and pentane-2,4-dione, Hpd (both Hopkins and Williams Ltd.) were used as supplied. A small amount of black impurity present in commercial thallium(I) ethoxide (Eastman–Kodak Co.) was removed prior to the addition of ethanol and Hpd for the preparation of Tl(pd). The insoluble product was recrystallised twice from methylene dichloride. Non-aqueous solvents were used either as

---

[28] K. W. Bagnall and D. Brown, *J. Chem. Soc.*, 1964, 3021.

[29] D. Brown and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1971, 81.

[30] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1966, 874.

[31] K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.* (*A*), 1966, 737.

[32] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1967, 719.

[33] J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143.

supplied or flushed with nitrogen and stored in contact with degassed molecular sieves in an inert-atmosphere box.

*Trichlorobis(pentane-*2,4-*dionato)protactinium*(V).— Protactinium pentachloride (0·05—0·1 g) was treated with an excess of Hpd (0·15 cm^3) dissolved in anhydrous methylene dichloride (0·5 cm^3). Addition of isopentane (1 cm^3) to the solution resulted in formation of needle crystals of the bright yellow *product*. These were washed on a filter stick with a mixture of isopentane and methylene dichloride and dried *in vacuo* at room temperature {Found: Cl, 19·7; Pa, 43·05. $[PaCl_3(pd)_2]$ requires Cl, 19·85; Pa, 43·15%}, yield *ca.* 70%.

*Tetrakis(pentane-*2,4-*dionato)protactinium*(IV).— Protactinium tetrachloride (0·01—0·03 g) was dissolved in oxygen-free ethanol (0·5 cm^3) and the stoicheiometric amount (1 : 4) of Tl(pd) added. Precipitated thallium(I) chloride was removed by centrifugation and washed with ethanol (0·5 cm^3). The combined supernatants were vacuum evaporated to dryness and the *product* extracted into boiling oxygen-free cyclohexane (1—2 cm^3) from which purple needles of β-$[Pa(pd)_4]$ crystallised at room temperature. Alternatively, the same crystal modification was obtained by dissolving the crude product in isopentane (2—5 cm^3) followed by cooling to −100 °C {Found: Pa, 38·5. $[Pa(pd)_4]$ requires Pa, 36·8%}. The product was also identified by *X*-ray powder-diffraction analysis which showed it to be isostructural with β-$[U(pd)_4]$; yields were *ca.* 80%.

Tetrakis(1,3-*diphenylpropane*-1,3-*dionato)protactinium*(IV).—The salt $[Et_4N]_2[PaCl_6]$ (0·01—0·02 g) was stirred with the stoicheiometric quantity (1 : 4) of Tl(dppd) in oxygen-free methylene dichloride. The resulting dark green solution was removed from precipitated TlCl by centrifugation and evaporated *in vacuo* to yield a green oil, which was induced to solidify by grinding under isopentane (3 × 1 cm^3). The product was extracted into oxygen-free benzene from which it was recovered as dark green crystals by vacuum evaporation of the solvent. *X*-Ray powder-diffraction analysis showed the product to be isostructural with $[U(dppd)_4]$.

*Tetrakis(pentane-*2,4-*dionato)-zirconium*(IV), *-hafnium*(IV), *and -thorium*(IV).—The appropriate tetrachloride [0·2—1·0 g; or, additionally in the case of zirconium, $Zr(O)Cl_2,8H_2O$] was dissolved in hot ethanol to which was added stoicheiometric amounts of Hpd and piperidine (1 : 4 : 4 mol ratio MCl_4 : Hpd : pip). The complexes β-$[Zr(pd)_4]$ and α-$[Th(pd)_4]$, which crystallised on cooling, were washed with cold ethanol (1 cm^3) and vacuum dried at room temperature. The ethanolic solution of $[Hf(pd)_4]$ was evaporated to dryness and the product extracted into benzene; following removal of the benzene by vacuum evaporation, β-$[Hf(pd)_4]$ was obtained by recrystallisation from the minimum volume of hot ethanol {Found: Zr, 19·05; Th, 36·95. $[Zr(pd)_4]$ and $[Th(pd)_4]$ require, respectively, Zr, 18·7 and Th, 36·9%}. The crystal modifications and β-$[Hf(pd)_4]$ were identified by *X*-ray powder-diffraction analysis.

*Tetrakis(pentane-*2,4-*dionato)uranium*(IV).—A reaction similar to that employed for the preparation of $[Pa(pd)_4]$ but with benzene as the solvent was used to prepare $[U(pd)_4]$. The product was isolated by vacuum evaporation of the supernatant and combined benzene washings of the precipitated TlCl after allowing up to 24 h for completion of the reaction {Found: U, 37·35. $[U(pd)_4]$ requires U, 37·5%}. *X*-Ray powder-diffraction analysis indicated that α-$[U(pd)_4]$ was obtained under these conditions. Recrystallisation from hot cyclohexane yielded β-$[U(pd)_4]$.

*Tetrakis(pentane-*2,4-*dionato)plutonium*(IV).—Benzene (3 cm^3) containing an excess of Hpd (0·1 cm^3) was added to tris(pentane-2,4-dionato)plutonium(III) (0·05 g). When oxygen was bubbled through the resulting solution a rapid colour change, green ⟶ red, occurred; β-$[Pu(pd)_4]$ was isolated by vacuum evaporation of the benzene solution at room temperature. The *product*, obtained as well formed, plate-like, crystals, was identified by single-crystal *X*-ray diffraction studies.

*Tris(pentane-*2,4-*dionato)plutonium*(III).— Plutonium metal (0·15 g) was dissolved in *ca.* 1M-$HClO_4$ (5 cm^3).* Nitrogen was bubbled through the resulting solution and Hpd (0·3 cm^3) dissolved in 1M-NH_4OH (6 cm^3) was added. The green *product* was washed with water, vacuum dried, and recrystallised from benzene. The product was identified by *X*-ray powder-diffraction analysis which showed it to be isostructural with $[Nd(pd)_3]$.

Analyses.—Metals were determined by ignition to the dioxide (Zr, Hf, or Th) or in the case of uranium, U_3O_8, following destruction of the tetrakis(pentane-2,4-dionates) by heating with concentrated nitric acid. Protactinium and americium were determined by a combination of α assay and α-pulse analysis (specific activities:[34,35] Pa, 1·062 × 10^8; ^{241}Am, 7·606 × 10^9 α disintegrations min^{-1} mg^{-1}) of aliquot portions of a concentrated nitric acid solution containing the complex or (Pa) by ignition of the hydrated oxide (to Pa_2O_5) obtained by addition of aqueous ammonia to $[PaCl_3(pd)_2]$. In the latter instance, chloride in the supernatant was precipitated and weighed as AgCl.

Physical Measurements.—*X*-Ray powder[36] and single-crystal Weissenberg[37] and precession photographs were recorded as described previously. Observed powder reflections were indexed by comparison with the pattern calculated for β-$[U(pd)_4]$ using the program Genstruck[38] and available unit-cell parameters. The indexed $\sin^2\theta$ values were refined and unit-cell constants calculated by means of the program Cohen.[38] I.r. spectra were recorded for Nujol mulls of the complexes between potassium bromide plates using either a Hilger-Watts Infrascan instrument or a Perkin-Elmer model 157, and between Polythene plates using either Grubb Parsons DM4 (690—225 cm^{-1}) or Perkin-Elmer 180 spectrometers (520—50 cm^{-1}). Spectra were also recorded in the range 400—40 cm^{-1} using a Beckmann interferometer with wave analyser, the samples being pressed in a low-m.p. paraffin wax. Solid-state spectra (400—20 000 cm^{-1}) were recorded as described previously.[39]

We thank Dr. C. E. F. Rickard for assistance with the single-crystal studies on $[PaCl_3(pd)_2]$, Mrs. K. M. Glover for provision of α-spectrometry facilities, and Mr. A. M. Deane for provision of spectral facilities.

[4/1088 *Received, 4th June,* 1974]

---

* 1M = 1 mol dm^{-3}.

[34] D. Brown, S. N. Dixon, K. M. Glover, and F. J. G. Rogers, *J. Inorg. Nuclear Chem.*, 1968, **30**, 19.

[35] F. L. Oetting and S. R. Gunn, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2659.

[36] D. Brown, T. L. Hall, and P. T. Moseley, *J.C.S. Dalton*, 1973, 686.

[37] P. T. Moseley, D. Brown, and B. Whittaker, *Acta Cryst.*, 1972, **B28**, 1816.

[38] J. A. C. Marples and J. L. Shaw, Brit. Report AERE-R 5210, 1966.

[39] D. Brown, B. Whittaker, and J. Edwards, Brit. Report AERE-R 7480 1972.