Some Oxygen-donor Complexes of Acetylacetonatotrichlorothorium(IV), Bis(acetylacetonato)-dichloro- and -di-*N*-thiocyanato-thorium(IV) and -uranium(IV)

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The oxygen-donor complexes [$Th(acac)Cl_3(dipiba)_2$] (Hacac = $MeCOCH_2COMe$, dipiba = $Me_2CHCONPr^i_2$), [$Th(acac)_2Cl_2(thf)_2$] (thf = tetrahydrofuran), [$U(acac)_2Cl_2(dipiba)$], and [$M(acac)_2(NCS)_2L_2$] (M = Th or U; L = thf, dipiba, $EtCONPr^i_2$, or PPr^i_3O) have been prepared. The i.r., near i.r.–visible [uranium(IV) compounds only], and ^1H n.m.r. spectra [thorium(IV) compounds only] are reported, and using a cone-packing model their stoicheiometries are discussed in terms of the steric crowding about the metal atom.

Bis(acetylacetonato)dichlorouranium(IV) complexes of composition [$U(acac)_2Cl_2L_2$] have been reported[1] with L = tetrahydrofuran (thf), 1,2-dimethoxyethane, triphenylphosphine oxide, 1,10-phenanthroline, and 2,2′-bipyridine. The complex [$U(acac)_2Cl_2(thf)_2$] loses thf when stirred with n-pentane,[2] behaviour which is consistent with overcrowding around the metal atom for, on the cone-packing model,[3] the values of Σc.a.f. (c.a.f. = cone angle factor) for complexes of the type [$U(acac)_2Cl_2L_2$] lie between 0.86 and 0.90 whereas those for the mono complexes [$U(acac)_2Cl_2L$] would lie between 0.76 and 0.79, within the 'stable' range observed for uranium(IV) complexes of known structure.[3] However, bis complexes would be expected when chloride ions (c.a.f. = 0.14) are replaced by the smaller NCS groups (c.a.f. = 0.11). Since the radius of the thorium(IV) ion (1.02 Å) is appreciably larger than that of uranium(IV) (0.97 Å), complexes of the type [$Th(acac)_2Cl_2L_2$] (Σc.a.f. = 0.81—0.84) would be expected to be more stable with respect to loss of the ligand L than the uranium(IV) analogues. Thorium complexes of this type do not appear to have been recorded, and it was therefore of interest to investigate the formation of both thorium(IV) and uranium(IV) complexes of the types [$M(acac)_2Cl_2L_x$] and [$M(acac)_2(NCS)_2L_x$].

Experimental

All of the experimental work, including the drying of solvents and the handling of the air- and moisture-sensitive starting materials and products, was carried out as described previously.[4–6]

Materials.—The compounds $ThCl_4$,[7] UCl_4,[8] $ThCl_4$·3dipiba, UCl_4·2dipiba (dipiba = $Me_2CHCONPr^i_2$),[9] $ThCl_4$·3dippa (dippa = $EtCONPr^i_2$),[9] $ThCl_4·2PPr^i_3O$,[10] PPr^i_3O[11] and the amides used as ligands[4] were prepared by the published methods.

Preparation of the Complexes.—(*a*) [$Th(acac)_2Cl_2(thf)_2$]. This was prepared by adding a slight excess of solid Na(acac) (0.85 g, 7 mmol) to a solution of $ThCl_4$ (1.2 g, 3.3 mmol) in thf (15 cm^3). After stirring for 24 h, the supernatant was vacuum evaporated to an oily residue which was dissolved in dichloromethane (10 cm^3); the filtrate was then vacuum evaporated to an oil which solidified when ground under n-hexane. The resulting yellowish white solid was dissolved in thf (10 cm^3) and vacuum evaporated to *ca.* 3 cm^3, when the product began to separate as colourless crystals. The supernatant was discarded after standing overnight, and the crystalline *product* was washed with n-hexane (2 × 3 cm^3) then with n-pentane (3 × 3 cm^3) and vacuum dried (10 h).

(*b*) [$U(acac)_2Cl_2(dipiba)$]. This was prepared by adding a slight excess of solid Na(acac) (0.18 g, 1.5 mmol) to a solution of UCl_4·2dipiba (0.5 g, 0.7 mmol) in dichloromethane (10 cm^3). After stirring overnight, the supernatant was vacuum evaporated to an oily residue which solidified on grinding under n-pentane to yield an orange *solid.* This was washed with n-pentane (2 × 3 cm^3) and vacuum dried (8 h).

(*c*) [$Th(acac)_2(NCS)_2(thf)_2$]. This was prepared by adding the stoicheiometric quantity of KNCS (0.26 g, 2.7 mmol) to a solution of $ThCl_4$ (0.5 g, 1.34 mmol) in thf (10 cm^3). After stirring for 24 h, a slight excess of Na(acac) (0.35 g, 2.85 mmol) was added, and the mixture was stirred for a further 24 h, after which the supernatant was vacuum evaporated to an oily residue. This was dissolved in dichloromethane (10 cm^3) and the filtrate was vacuum evaporated to an oil which was dissolved in thf (4 cm^3). n-Pentane was then added until the solution became cloudy; the cloudiness was removed by dropwise addition of thf. The *product* separated as colourless crystals on standing overnight.

The complex [$U(acac)_2(NCS)_2(thf)_2$] was prepared in the same way from UCl_4 except that the vacuum evaporation of the supernatant from the reaction mixture to dryness yielded a green solid. This was redissolved in thf (10 cm^3) and the filtrate was vacuum evaporated to *ca.* 3 cm^3. On standing for 3 d the *product* separated as large green crystals. The complexes [$Th(acac)_2(NCS)_2(PPr^i_3O)_2$] and [$Th(acac)_2(NCS)_2$(dipiba)$_2$] were prepared from $ThCl_4·2PPr^i_3O$ and $ThCl_4$·3dipiba in the same way except that the supernatant from the reaction mixture was vacuum evaporated to *ca.* 3 cm^3; on standing overnight the *products* separated as large white crystals. The complex [$Th(acac)_2(NCS)_2(dippa)_2$] was also prepared similarly from $ThCl_4$·3dippa except that vacuum evaporation of the dichloromethane solution to dryness left a honeycombed residue which solidified on standing overnight under n-pentane. These *products* were each washed with n-pentane (3 × 3 cm^3) and vacuum dried (10 h).

(*d*) [$U(acac)_2(NCS)_2(dippa)_2$]. This was prepared by adding an excess of dippa (0.25 g, 1.6 mmol) in dichloromethane (5 cm^3) to a solution of [$U(acac)_2(NCS)_2(thf)_2$] (0.5 g, 0.7 mmol) in the same solvent (5 cm^3). After stirring for 15 min the dark green solution was vacuum evaporated almost to dryness, when the *product* separated as a dark green crystalline solid. This was washed with a mixture of n-pentane and dichloromethane (3:1, v/v; 2 × 3 cm^3) then with n-pentane (3 × 3 cm^3) and vacuum dried (8 h). Dark green [$U(acac)_2(NCS)_2(dipiba)_2$] was prepared in the same way and green [$U(acac)_2(NCS)_2$-

Table 1. Analytical results (%) with calculated values in parentheses

Complex	M	C	H	N	S	Yield (%)
[Th(acac)$_2$Cl$_2$(thf)$_2$][a]	35.9 (36.0)	33.6 (33.5)	4.8 (4.7)			*ca.* 70
[Th(acac)Cl$_3$(dipiba)$_2$][b]	30.8 (29.8)	38.3 (38.5)	6.4 (6.3)	3.3 (3.6)		*ca.* 45
[U(acac)$_2$Cl$_2$(dipiba)][c]	34.6 (35.1)	35.4 (35.4)	5.2 (5.2)	2.2 (2.1)		*ca.* 78
[Th(acac)$_2$(NCS)$_2$(thf)$_2$]	33.6 (33.6)	34.1 (34.8)	4.3 (4.3)	3.9 (4.1)	8.7 (9.3)	*ca.* 76
[U(acac)$_2$(NCS)$_2$(thf)$_2$]	33.8 (34.2)	34.5 (34.5)	4.5 (4.3)	4.0 (4.0)	9.2 (9.2)	*ca.* 62
[Th(acac)$_2$(NCS)$_2$(dipiba)$_2$]	26.5 (26.1)	42.7 (43.2)	6.3 (6.3)	6.2 (6.3)	6.7 (7.2)	*ca.* 82
[U(acac)$_2$(NCS)$_2$(dipiba)$_2$]	26.6 (26.6)	42.0 (42.9)	6.2 (6.3)	6.2 (6.3)	7.7 (7.2)	*ca.* 70
[Th(acac)$_2$(NCS)$_2$(dippa)$_2$]	27.2 (27.0)	41.0 (41.9)	6.0 (6.0)	6.4 (6.5)	7.2 (7.4)	*ca.* 72
[U(acac)$_2$(NCS)$_2$(dippa)$_2$]	27.4 (27.5)	41.2 (41.6)	6.0 (6.0)	6.3 (6.5)	7.4 (7.4)	*ca.* 85
[Th(acac)$_2$(NCS)$_2$(PPr$^i_3$O)$_2$][d]	25.8 (25.8)	39.8 (40.1)	6.45 (6.2)	3.1 (3.1)	7.1 (7.1)	*ca.* 80
[U(acac)$_2$(NCS)$_2$(PPr$^i_3$O)$_2$][e]	26.4 (26.3)	38.9 (39.8)	6.3 (6.2)	3.1 (3.1)	7.7 (7.1)	*ca.* 92

[a] Cl 11.0 (11.0)%. [b] Cl 13.4 (13.7)%. [c] Cl 10.6 (10.5)%. [d] P 6.9 (6.9)%. [e] P 7.2 (6.9)%.

Table 2. I.r. data (cm^{-1}) for the complexes[a]

	acac		Ligand[b]				
Complex	ν(CO)	ν_{asym}(CC)	ν(X=O)	$\Delta\nu$(X=O)	thf modes	ν(CN)	ν(M–Cl)[c]
Th(acac)$_4$	1 574s	1 518s					
[Th(acac)$_2$Cl$_2$(thf)$_2$]	1 568s	1 519s			876m, 840w (sh)		240s
[Th(acac)Cl$_3$(dipiba)$_2$]	1 590s	1 523s (sh)	1 545s	86			250s, 242s (sh)
[Th(acac)$_2$(NCS)$_2$(thf)$_2$]	1 565s, br	1 520s			860s, 840m (sh)	2 015s	
[Th(acac)$_2$(NCS)$_2$(dippa)$_2$]	1 568s	1 518s	1 550s (sh)	84		2 058 (sh), 2 041s	
[Th(acac)$_2$(NCS)$_2$(dipiba)$_2$]	1 580s	1 519s	1 543s (sh)	88		2 052s	
[Th(acac)$_2$(NCS)$_2$(PPr$^i_3$O)$_2$]	1 577s	1 511s	1 098s (sh), 1 080s	75, 66		2 038s	
U(acac)$_4$	1 576s	1 516s					
[U(acac)$_2$Cl$_2$(dipiba)]	1 563s (sh)	1 516s	1 546s (sh)	85			258s
[U(acac)$_2$(NCS)$_2$(thf)$_2$]	1 558s	1 515s			862m, 841m (sh)	2 019s	
[U(acac)$_2$(NCS)$_2$(dippa)$_2$]	1 572s (sh)	1 519s	1 559s	75		2 062s (sh), 2 048s	
[U(acac)$_2$(NCS)$_2$(dipiba)$_2$]	1 569s (sh)	1 517s (sh)	1 545s	86		2 046s	
[U(acac)$_2$(NCS)$_2$(PPr$^i_3$O)$_2$]	1 578s	1 513s	1 097s (sh), 1 076s	76, 70		2 042s	

[a] s = Strong, m = medium, w = weak, sh = shoulder, and br = broad. [b] X = C or P. [c] M = Th or U.

(PPr$^i_3$O)$_2$] was prepared similarly, except that vacuum evaporation of the reaction mixture yielded a green oil which solidified on standing overnight under n-pentane (10 cm^3). The green crystalline product was washed with n-pentane (3 × 3 cm^3) and vacuum dried.

(*e*) [Th(acac)Cl$_3$(dipiba)$_2$]. This was obtained in an attempt to prepare [Th(acac)$_2$Cl$_2$(dipiba)$_2$] by treating [Th(acac)$_2$Cl$_2$(thf)$_2$] (0.5 g, 0.78 mmol) with an excess of dipiba (0.4 g, 2.3 mmol) in thf (10 cm^3). After vacuum evaporation of the solution to *ca.* 4 cm^3, n-pentane was added until the solution became cloudy. The white *product*, which crystallised on standing for *ca.* 2 h, was washed with n-pentane and vacuum dried (8 h).

The analytical results are summarised in Table 1.

Physical Measurements.—I.r., near i.r.–visible,[12] and ^{1}H n.m.r. spectra [6] were obtained as described previously.

Results and Discussion

The Complexes.—The complex [Th(acac)$_2$Cl$_2$(thf)$_2$] was obtained by treating ThCl$_4$ in thf with a slight excess of Na(acac) and [U(acac)$_2$Cl$_2$(dipiba)] was prepared in a similar manner from UCl$_4$·2dipiba in dichloromethane. The attempted preparation of [Th(acac)$_2$Cl$_2$(dipiba)$_2$] from [Th(acac)$_2$Cl$_2$(thf)$_2$] with an excess of dipiba in thf yielded [Th(acac)Cl$_3$(dipiba)$_2$], presumably as a result of disproportionation (see below). The complexes [M(acac)$_2$(NCS)$_2$(thf)$_2$] and [Th(acac)$_2$(NCS)$_2$L$_2$] (L = dippa, dipiba, or PPr$^i_3$O) were prepared from the metal tetrachlorides (thf complexes), ThCl$_4$·3L (L = dippa or dipiba), and ThCl$_4$·2PPr$^i_3$O respectively by reaction with the stoicheiometric quantity of potassium thiocyanate in thf, whereas the complexes [U(acac)$_2$(NCS)$_2$L$_2$] (L = dippa, dipiba, or PPr$^i_3$O) were prepared by treating [U(acac)$_2$(NCS)$_2$(thf)$_2$] with an excess of the appropriate ligand in dichloromethane. The uranium(IV) complexes were green or dark green in colour, excepting [U(acac)$_2$Cl$_2$(dipiba)] which was orange, an unusual colour for a uranium(IV) complex.

The bis complex [U(acac)$_2$Cl$_2$(dipiba)$_2$] could not be obtained; this complex would be overcrowded in cone-packing terms [3] (Σc.a.f. = 0.88) and the bulky dipiba ligand would also contribute a relatively high degree of second-order crowding (see ref. 3) which would increase the value of Σc.a.f. The value of Σc.a.f. for [U(acac)$_2$Cl$_2$(dipiba)] is 0.77, excluding second-order contributions, which is within the limits[3] (Σc.a.f. = 0.80 ± 0.03) for stable complexes. Similarly, [Th(acac)$_2$Cl$_2$(dipiba)$_2$]

Table 3. Principal features (nm) in the near i.r.–visible spectra of the uranium(IV) complexes (600—2 200 nm)

Complex	Solid reflectance	Dichloromethane solution	Tetrahydrofuran solution
$U(acac)_4$	650s, 830w, 975w (sh), 1 060s (sh), 1 110s, 1 420m, br, 1 670m		650s, 670m (sh), 820w, 1 040m (sh), 1 135s, br, 1 360m, br, 1 660w
$[U(acac)_2Cl_2(dipiba)]$	645m, 858s, 1 043s, 1 135m, 1 315s, 1 520m, 1 950m	658s, 862m, 1 054s, 1 140s (sh), 1 328m, 1 522m, 1 974m	660s, 850w, 1 056s (sh), 1 138s, 1 320m, 1 540w, 1 945w
$[U(acac)_2(NCS)_2(dipiba)_2]$	675m, 815w, 1 065s (sh), 1 128s, 1 362m, 1 510m (sh)	667s, 805vw, 1 126s, 1 354m, 1 510w (sh)	662m, 820w, 1 038m (sh), 1 128s, 1 320m, 1 444w (sh)
$[U(acac)_2(NCS)_2(dippa)_2]$	670m, 810w, 1 060s (sh), 1 120s, 1 355m, 1 482m (sh)	680m, 820w, 1 054w (sh), 1 122s, 1 350m (sh), 1 490m	666m, 822w, 1 042m, 1 136s, 1 324m, 1 446w (sh)
$[U(acac)_2(NCS)_2(thf)_2]$	640m, 800m, 1 020s (sh), 1 118s, 1 300m, 1 523w	660m, 815w, 1 040s (sh), 1 130s, 1 335m	655m, 810w, 1 035m (sh), 1 120s, 1 300m, 1 435w (sh)
$[U(acac)_2(NCS)_2(PPr^i_3O)_2]$	680m, 878w, 1 055m (sh), 1 123s, 1 490m, br, 1 670w (sh)	678s, 870vw, 1 054m (sh), 1 126s, 1 500m, br	680s, 860w, 1 058m (sh), 1 130s, 1 520m, br

Relative intensities: s = strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad.

Table 4. ^1H N.m.r. spectra[a] of the complexes in $CDCl_3$

				$[Th(acac)_2(NCS)_2L_2]$			
Proton assignments	$Th(acac)_4$	$[Th(acac)Cl_3(dipiba)_2]$	$[Th(acac)_2Cl_2(thf)_2]$[b]	L = thf	dippa	dipiba	PPr^i_3O
$[C\mathit{H}_3COCHCOC\mathit{H}_3]^-$	1.87 (24 H, s)	1.94 (6 H, s)	2.03 (12 H, s)	2.0 (12 H, s)	1.89 (12 H, s)	1.91 (12 H, s)	1.85 (12 H, s)
$[CH_3COC\mathit{H}COCH_3]^-$	5.34 (4 H, s)	5.57 (1 H, s)	5.60 (2 H, s)	5.59 (2 H, s)	5.47 (2 H, s)	5.49 (2 H, s)	5.38 (2 H, s)
$C\mathit{H}_2C\mathit{H}_2CH_2OCH_2$			1.88 (8 H, m)	1.95 (8 H, m)			
$CH_2CH_2C\mathit{H}_2OC\mathit{H}_2$			3.93 (8 H, m)	4.14 (8 H, m)			
$C\mathit{H}_3CH_2CO$					1.26 (t, J = 7)		
$[(C\mathit{H}_3)_2CH]_2N$					1.34 (d, J = 7) 1.41 (d, J = 7) (30 H)		
$CH_3C\mathit{H}_2CO$					2.67 (4 H, q, J = 7)		
$[(CH_3)_2C\mathit{H}]_2N$					4.01 (4 H, m, J = 7)		
$(C\mathit{H}_3)_2CHCON[CH(C\mathit{H}_3)_2]_2$		1.27 (d, J = 7) 1.42 (d, J = 7) (36 H)				1.28 (d, J = 7) 1.40 (d, J = 7) (36 H)	
$(CH_3)_2C\mathit{H}CON[CH(CH_3)_2]_2$		2.91 (2 H, m, J = 7)				2.87 (2 H, m, J = 7)	
$(CH_3)_2CHCON[C\mathit{H}(CH_3)_2]_2$		3.77 (4 H, m, J = 7)				3.84 (4 H, m, J = 7)	
$[(C\mathit{H}_3)_2CH]_3PO$							1.27 (18 H, d, J = 7) 1.44 (18 H, d, J = 7)
$[(CH_3)_2C\mathit{H}]_3PO$							2.43 (6 H, m, J = 7)

[a] Chemical shifts (p.p.m.) relative to $SiMe_4$; proton integrations and J values (Hz) in parentheses. s = Singlet, d = doublet, m = multiplet, q = quartet, and t = triplet. [b] Recorded in CD_2Cl_2.

(Σc.a.f. at least 0.84) could not be isolated and the only product obtained, $[Th(acac)Cl_3(dipiba)_2]$ (Σc.a.f. = 0.78), presumably results from the disproportionation $3[Th(acac)_2Cl_2(dipiba)_2] \longrightarrow Th(acac)_4 + 2[Th(acac)Cl_3(dipiba)_2] + 2dipiba$. In contrast, $[U(acac)_2(NCS)_2(dipiba)_2]$ and $[Th(acac)_2(NCS)_2(dipiba)_2]$ (Σc.a.f. at least 0.82 and 0.78 respectively) were readily obtained, as were the analogous complexes with dippa and PPr^i_3O, for which the minimum values of Σc.a.f. are similar to those of the dipiba complexes.

X-Ray powder diffraction photographs of $[U(acac)_2(NCS)_2(thf)_2]$ and $U(acac)_4$ indicated that none of the latter was present in the thf complex, so that the complex is not a mixture of disproportionation products such as $U(acac)_4$ and $U(NCS)_4{\cdot}4thf$.

All of the complexes are very soluble in dichloromethane but are less soluble in thf and are insoluble in n-pentane. The thf complexes, $[M(acac)_2(NCS)_2(thf)_2]$ (M = Th or U) and $[Th(acac)_2Cl_2(thf)_2]$, are more hygroscopic than $[U(acac)_2Cl_2$-

(dipiba)] and $[Th(acac)Cl_3(dipiba)_2]$, and, in turn, these complexes are much more hygroscopic than $[M(acac)_2(NCS)_2L_2]$ (M = Th or U; L = dippa, dipiba, or PPr^i_3O).

I.r. Spectra.—In the i.r. spectra of the complexes (Table 2) the shifts in $\nu(CO)$ of the amides and of $\nu(PO)$ of PPr^i_3O are similar in magnitude to the shifts observed in the spectra of the corresponding complexes of the tetrachlorides[9,10] and tetra-*N*-thiocyanates.[13] Table 2 also includes data for the known compounds $M(acac)_4$ (M = Th or U) for comparison in respect of the features assigned to $\nu(CO)$ and $\nu_{asym}(CC)$ of the bonded acetylacetonate groups. The CN stretching mode in the thiocyanate compounds appears at 2 015—2 062 cm^{-1}, consistent with N-bonding of the thiocyanate groups[14] and the relatively high intensity of this feature also suggests N-bonding.[15,16] The C–S mode, which should appear at 760—880 cm^{-1} in the i.r. spectra of nitrogen-bonded thiocyanates or at 700 cm^{-1} for sulphur-bonded thiocyanates,[17,18] could not be identified in the spectra because of interference from modes arising from the organic ligands.

Near I.r.–Visible Spectra.—The principal features in the near i.r.–visible spectra of the uranium(IV) complexes are summarised in Table 3. The spectra of the complexes $[U(acac)_2(NCS)_2L_2]$ (L = thf, dippa, dipiba, or PPr^i_3O) in dichloromethane and in thf solution are almost identical and are also very similar to their solid reflectance spectra. All of these spectra are consistent with the presence of high (> 6) co-ordination number uranium(IV) species (strong features at 1 020—1 060 and 1 118—1 135 nm). The solid reflectance spectrum of $[U(acac)_2Cl_2(dipiba)]$ is similar to its spectrum in dichloromethane solution, with two well separated features at 1 315 and 1 520 nm (solid reflectance) and 1 328 and 1 522 nm (dichloromethane solution), together with a relatively high intensity feature at 858 and 862 nm respectively. The spectra of this complex are very similar to that recorded[19] for $[U(acac)_2Cl_2(thf)]$ but differ from the spectra of the complexes $[U(acac)_2(NCS)_2L_2]$, as is also indicated by their different colour, and the main features are at similar wavelengths to those observed in the spectra of seven-co-ordinate uranium(IV) complexes such as $[U(NCS)_4(dmiba)_3]$[20] (dmiba ≡ $Me_2CHCONMe_2$). The two features observed in the region 1 000—1 150 nm also suggest the presence of other highly (> 6) co-ordinated uranium(IV) species, but these differ from those observed in the spectra of the complexes $[U(acac)_2(NCS)_2L_2]$ in their relative intensities; in the solid reflectance and dichloromethane solution spectra of $[U(acac)_2Cl_2(dipiba)]$ the feature at < 1 100 nm is stronger than that at > 1 100 nm. The presence of features at 1 950 (solid reflectance) and at 1 974 nm (dichloromethane solution) may indicate the presence of a six-co-ordinate uranium(IV) centre, which might suggest that $[U(acac)_2Cl_2(dipiba)]$ is partially disproportionated to a mixture of $U(acac)_4$ and $UCl_4 \cdot 2dipiba$. However, the colours of these last two complexes are green and bluish green respectively, whereas $[U(acac)_2Cl_2(dipiba)]$ is orange. A comparison of the solid reflectance and dichloromethane solution spectra of $[U(acac)_2Cl_2(dipiba)]$ with those of $U(acac)_4$ showed that the latter was not present, which indicates that the former is a genuine compound.

The spectrum of $[U(acac)_2Cl_2(dipiba)]$ in thf was almost identical to those of the complexes $[U(acac)_2(NCS)_2L_2]$, with the strongest feature at 1 138 nm, suggesting that solvation and ligand dissociation occur in that solvent: $[U(acac)_2Cl_2(dipiba)] \rightleftharpoons [U(acac)_2Cl_2(dipiba)(thf)] \rightleftharpoons [U(acac)_2Cl_2(thf)_2]$ + dipiba. The i.r. spectrum of the complex in thf shows a feature at 1 634 cm^{-1} due to free dipiba.

^1H *N.M.R. Spectra.*—The ^1H n.m.r. spectra of the complex $[Th(acac)_2Cl_2(thf)_2]$ in CD_2Cl_2 and of the other thorium(IV) complexes in $CDCl_3$ consist of singlet methyl and singlet chelate-ring proton (–CH=) resonances of the acac groups in addition to resonances due to the neutral ligands. The chemical shifts, including data for $Th(acac)_4$, are summarised in Table 4.

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