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Some β-Diketone Chelate Complexes with Uranium(IV), Thorium(IV), and Cerium(IV). Preparation and IR Spectra

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The tetrakis β-diketonates of U(IV), Th(IV), and Ce(IV) with acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone, dibenzoylmethane, benzoyltrifluoroacetone, and thenoyltrifluoroacetone have been prepared and their infrared spectra measured in the range 4000—200 cm^{-1}. In every chelate, a strong, broad and metal sensitive band related to the M–O stretching mode was found in the 200—250 cm^{-1} region.

Many β-diketones coordinate to various metal ions as a bidentate ligand, generally forming stable chelates. Acetylacetone and thenoyltrifluoroacetone are well-known as extraction reagent for various metal ions and as metal indicator in chelatometry. The β-diketonato chelates of actinoid and lanthanoid elements are of particular interest, since they are used as solvent extraction reagent for the actinoid elements in the reprocessing of spent fuel and the separation of actinoid elements from fission products.1) The possibility of their use as nuclear fuel with organic moderator has been suggested. Most β-diketonato chelates are so volatile that they are often purified by means of sublimation, and the volatility of the β-diketonates of uranium has been investigated from the view point of isotope separation.2)

The measurements of the infrared spectra for tetrakis β-diketonates of uranium(IV), thorium(IV), and cerium(IV) have been carried out for acetylacetonates and thenoyltrifluoroacetonates.3,4) Fay and Pinnavaia3) measured the IR and Raman spectra of $M(acac)_4$ (M=Zr(IV), Hf(IV), Ce(IV), and Th(IV)) and assigned the IR absorption bands in the 1600—500 cm^{-1} region according to the assignments for the

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1) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co., London (1957).

2) a) H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer, and R. A. Lad, *J. Amer. Chem. Soc.*, **75**, 2446 (1953). b) H. Gilman, R. G. Jones, E. Bindschardler, D. Blume, G. Karmas, G. A. Martin, Jr., J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *ibid.*, **78**, 2790 (1956). c) H. A. Swain, Jr. and D. G. Karraker, *Inorg. Chem.*, **9**, 1766 (1970).

3) R. C. Fay and T. J. Pinnavaia, *ibid.*, **7**, 508 (1968).

4) Y. Baskin and N. S. K. Prasad, *J. Inorg. Nucl. Chem.*, **25**, 1001 (1963).

β-diketonato chelates with transition metal ions reported by Behnke and Nakamoto.5) They also assigned some metal sensitive bands in the 500—70 cm^{-1} region to the M–O band. The IR study for the effect of replacement of the methyl groups of the acetylacetonates in the β-diketonato chelates with Cu(II) and Ni(II) has been made by Nakamoto *et al.*6)

This paper deals with the preparation of several tetrakis-β-diketonates of U(IV), Th(IV), and Ce(IV) with acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone, dibenzoylmethane, benzoyltrifluoroacetone and thenoyltrifluoroacetone and their IR spectra in the range 4000—200 cm^{-1} together with the substituent effects on the M–O bond.

Experimental

Preparation. Hydrochloric acid (6N) solution of U(IV) (supplied by Power Reactor and Nuclear Fuel Corporation, Tokai works) was used for preparation of uranium(IV) chelates. The solution contained 302.8 g U(IV) per liter. Thorium tetrachloride hydrate and cerium(IV) ammonium sulfate tetrahydrate, both of GR grade, were used for the preparation of thorium(IV) and cerium(IV) chelates, respectively. All the ligands and other reagents were of GR grade and used without further purification. As the U(IV) ion in solution is particularly sensitive towards oxidation, the syntheses and purification of U(IV) chelates were carried out in a dry box filled with argon or nitrogen gas. The seven β-diketonato ligands used are denoted by: acetylacetonato, acac; trifluoroacetylacetonato, tfac; hexafluoroacetylacetonato, hfac; benzoylacetonato, bzac; dibenzoylmethanato, dbm; benzoyltrifluoroacetonato, bfac; thenoyltrifluoroacetonato, TTA. The chelates of uranium(IV), thorium(IV) and cerium(IV) were prepared as follows.

(1) U(acac)$_4$, Th(acac)$_4$, and Ce(acac)$_4$. Acetylacetone was added to a dilute U(IV) hydrochloric acid solution, aqueous thorium tetrachloride solution and the aqueous cerium(IV) ammonium sulfate solution each with the metal ion to acetylacetone ratio 1:4. These solutions were then gradually neutralized with concd. aqueous ammonia. The precipitates were filtered off, washed with water and dried *in vacuo*. The products were recrystallized twice from benzene-petroleum ether or toluene–petroleum ether and dried *in vacuo*. Found: C, 37.81; H, 4.40; U, 37.60%. Calcd. for U(acac)$_4$ (slightly greenish brown): C, 37.86; H, 4.45; U, 37.52%. Found: C, 38.08; H, 4.58; Th, 36.2%. Calcd for Th(acac)$_4$ (white): C, 38.22; H, 4.49; Th, 36.92%. Found: C, 44.51; H, 5.14; Ce, 25.82%. Calcd for Ce(acac)$_4$ (brown): C, 44.77; H, 5.26; Ce, 26.11%.

(2) U(hfac)$_4$, Th(hfac)$_4$, and Ce(hfac)$_4$. The U(IV) ion, Th(IV) ion and Ce(IV) ion were extracted from dilute U(IV) hydrochloric acid solution, aqueous Th(IV) solution and aqueous Ce(IV) solution respectively with a hexafluoroacetylacetone benzene solution. The products crystallized from these benzene solutions were recrystallized twice from benzene and dried *in vacuo*. Found: C, 23.77; H, 0.88%. Calcd for U(hfac)$_4$ (brown): C, 22.53; H, 0.38%. Found: C, 21.13; H, 0.52%. Calcd for Th(hfac)$_4$ (white): C, 22.66; H, 0.38%. Found: C, 23.12; H, 0.63%. Calcd for Ce(hfac)$_4$ (brown): C, 24.81; H, 0.42%.

(3) U(tfac)$_4$, Th(tfac)$_4$, U(bfac)$_4$, Th(bfac)$_4$, U(bzac)$_4$, Th(bzac)$_4$, U(bdm)$_4$, Th(dbm)$_4$, and U(TTA)$_4$. The ethanol solution of ligand was added to aqueous Th(IV) solution or U(IV) hydrochloric acid solution diluted with water or ethanol (metal ion: ligand≒1:4). The precipitates thus obtained were filtered, washed with water, dried *in vacuo* and purified as in the case of acetylacetonates. Found: C, 28.17; H, 2.10%. Calcd for U(tfac)$_4$ (yellowish brown): C, 28.25; H, 1.90%. Found: C, 28.62; H, 2.18%. Calcd for Th(tfac)$_4$ (white): C, 28.45; H, 1.91%. Found: C, C, 44.24; H, 1.98%. Calcd for Th(bfac)$_4$ (pale orange): C, 43.97; H, 2.21%. Found: C, 43.66; H, 2.13%. Calcd for U(bfac)$_4$ (reddish brown): C, 43.73; H, 2.20%. Found: C, 54.58; H, 4.39; U, 27.15%. Calcd for U(bzac)$_4$ (reddish brown): C, 54.42; H, 4.11; U, 26.97%. Found: C, 55.02; H, 4.42; Th, 26.88%. Calcd for Th(bzac)$_4$ (white): C, 54.79; H, 4.14; Th, 26.47%. Found: C, 63.89; H, 3.88; U, 21.17%. Calcd for U(dbm)$_4$ (reddish brown): C, 63.71; H, 3.92; U, 21.05%. Found: C, 63.84; H, 3.85; Th, 20.6%. Calcd for Th(dbm)$_4$ (yellow): C, 64.05; H, 3.94; Th, 20.63%. Found: C, 34.34; H, 1.74%. Calcd for U(TTA)$_4$ (reddish brown): C, 34.23; H, 1.44%. Found: C, 34.79; H, 1.50%. Calcd for Th(TTA)$_4$ (pale yellow) :C, 34.42; H, 1.44%.

(4) Ce(tfac)$_4$, Ce(bfac)$_4$, Ce(bzac)$_4$, Ce(dbm)$_4$, and Ce(TTA)$_4$. The ethanol solution of ligand was added to aqueous Ce(IV) solution. The chelates thus formed were extracted from the crude precipitates with benzene or toluene. The products crystallized from these benzene or toluene solutions were purified as in the case of hexafluoroacetylacetonates. Found: C, 31.99; H, 2.40%. Calcd for Ce(tfac)$_4$ (buff brown): C, 31.92; H, 2.15%. Found: C, 47.51; H, 2.35%. Calcd for Ce(bfac)$_4$ (brownish purple): C, 48.01; H, 2.42%. Found: C, 60.48; H, 4.63; Ce, 18.3%. Calcd for Ce(bzac)$_4$ (brown): C, 61.21; H, 4.62; Ce, 17.86%. Found: C, 69.53; H, 4.49; Ce, 13.54%. Calcd for Ce(dbm)$_4$ (reddish brown): C, 69.75; H, 4.30; Ce, 13.56%. Found: C, 37.58; H, 1.51%. Calcd for Ce(TTA)$_4$ (reddish brown): C, 37.50; H, 1.57%.

Measurements. IR absorption spectra were recorded on Hitachi-Perkin-Elmer 225 (4000—250 cm^{-1}) and Hitachi EPI-L (700—200 cm^{-1}) IR grating spectrophotometers, using the technique of Nujol mull and HCB mull supported between caesium iodide plates.

Results and Discussion

The yield of U(IV) β-diketonates was quantitative by the present method. However, yields of Th(IV)- and Ce(IV)-β-diketonates were not quantitative because of the fact that Th(IV)- and Ce(IV)-ion are easily hydrolyzed and their hydrolyzed products are less soluble in water. Generally, the yields of metal chelates with acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone were lower than those with the other four ligands, benzoylacetone, dibenzoylmethane, benzoyltrifluoroacetone and thenoyltrifluoroacetone. The U(IV) β-diketonates were gradually oxidized and discolored in air at room temperature, except for the chelates with the ligand containing phenyl and thienyl groups which were relatively stable in air. It was found from the absorption spectra in visible region that U(acac)$_4$, U(tfac)$_4$, and U(hfac)$_4$ were not stable even in organic solution. All the U(IV) β-diketonates were kept in a vacuum container, and all operations involved in preparations and measurements were carried out as rapidly as possible.

Tetrakis-bidentate chelate, to which all tetrakis β-

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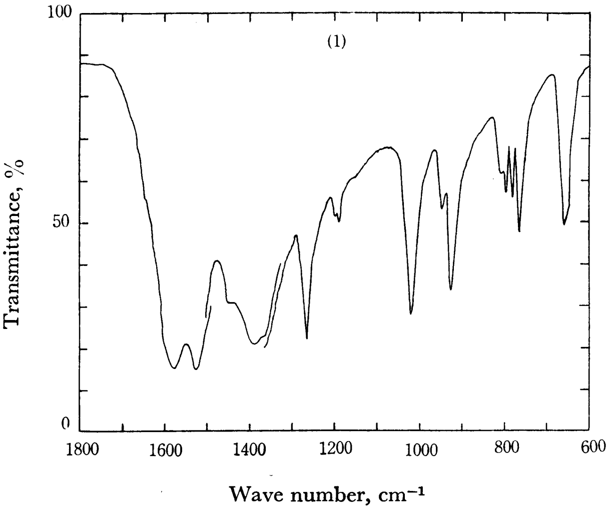
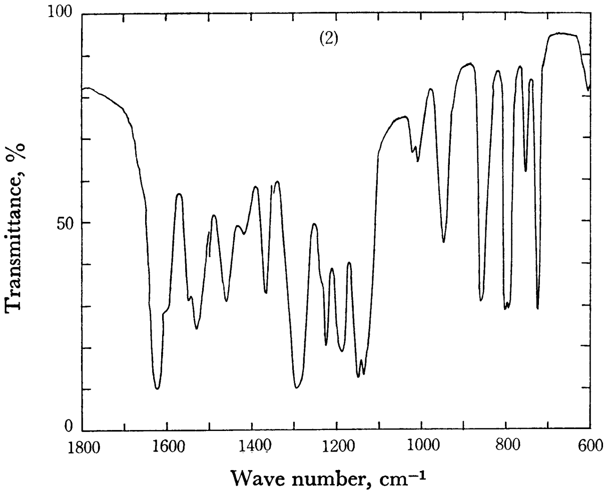
5) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

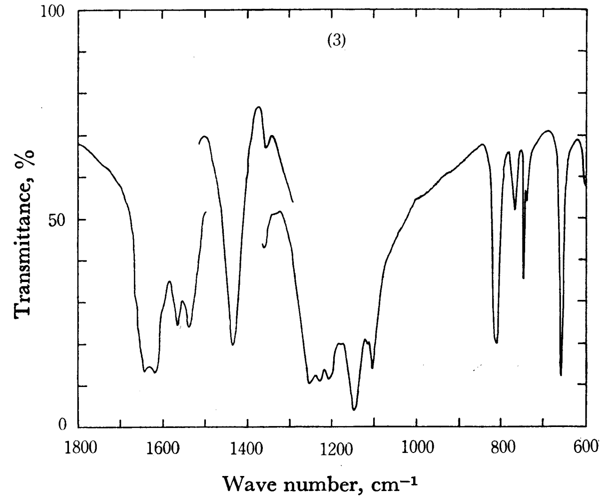
6) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

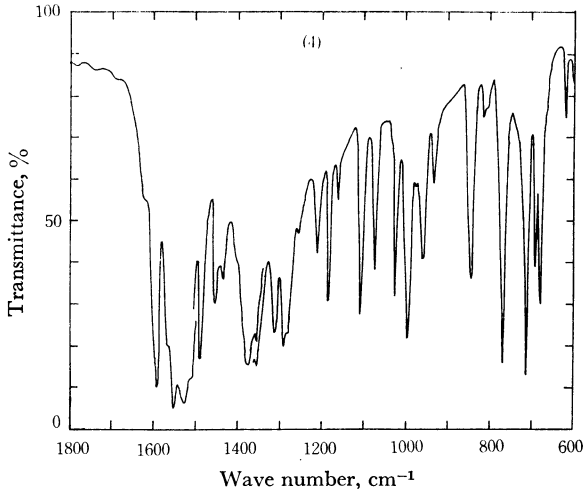
diketonato chelates belong, has the coordination number of eight around the central metal ion. The configuration of tetrakis β-diketonato chelates has been determined for two chelates $M(acac)_4$ (M=Zr, Ce, Th, and U)[7] and $M(dbm)_4$ (M=Ce, Th, and U)[8] to be square antiprism with D_2 symmetry and dodecahedron with D_{2d} symmetry, respectively. It seems that the tetrakis β-diketonato chelates with the other kind of ligand dealt with are also isomorphous for Ce(IV), Th(IV), and U(IV).

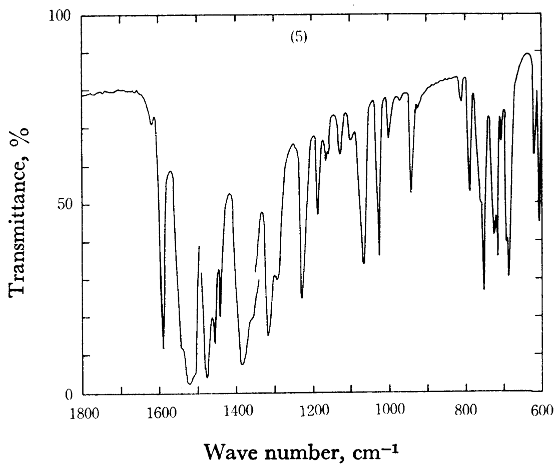
IR Spectra. In Fig. 1 are shown the IR spectra in the 1800—600 cm^{-1} region of $U(acac)_4$, $U(tfac)_4$, $U(hfac)_4$, $U(bzac)_4$, $U(dbm)_4$, $U(bfac)_4$, and $U(TTA)_4$ chelates. Above 1800 cm^{-1}, no absorption band is found except the C–H stretching bands (not given in the figure) of the methyl group, the γC–H bond, the phenyl group and the thienyl group near 3000 cm^{-1}.

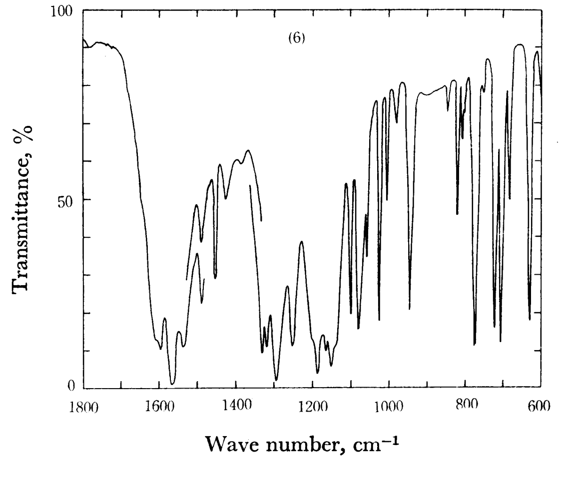












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7) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

8) V. L. Wolf and H. Barnighausen, *Acta Crystallogr.*, **13**, 778 (1960).

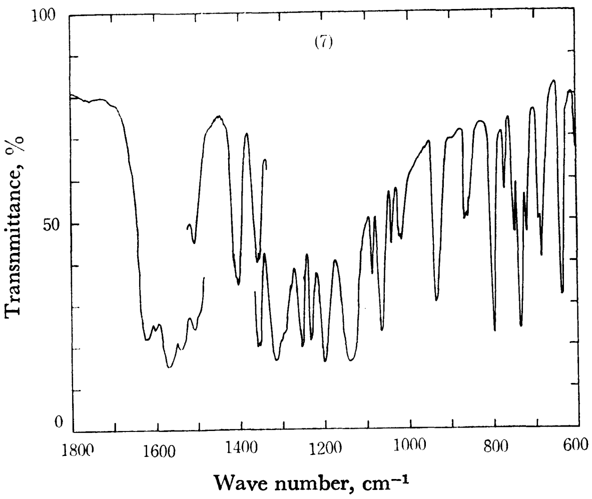

Fig. 1. Infrared spectra of the tetrakis β-diketonates of U(IV). (1) $U(acac)_4$, (2) $U(tfac)_4$, (3) $U(hfac)_4$, (4) $U(bzac)_4$, (5) $U(dbm)_4$, (6) $U(bfac)_4$, (7) $U(TTA)_4$.
200—1350, 1500—2700 cm^{-1}: Nujol mull. 1350—1500, 2700—4000 cm^{-1}: HCB mull.

The IR spectra of acetylacetonates of uranium reported by Lecomte[9] do not show the valence state of uranium. The present result differs from that given by Lecomte, but is in line with $Th(acac)_4$ given by Fay and Pinnavaia.[3] The spectra of $M(acac)_4$ (M= U(IV), Th(IV), and Ce(IV)) in the 1600—500 cm^{-1} region are very similar to each other and to those of $Pt(acac)_2$ and $Cu(acac)_2$.[5,10] They are independent of both mass and coordination number of the central metal ion. The absorption bands of each chelate in the 1700—500 cm^{-1} region can be assigned on the basis of β-diketonato chelates with bivalent- or trivalent-transition metal ion reported by Nakamoto *et al.*,[5,6] Mikami *et al.*,[10] and also based on the result reported by Fay and Pinnavaia.[3] The infrared frequencies and tentative assignments for $U(acac)_4$ are given in Table 1.

In the spectra of tetrakis β-diketonates other than tetrakis acetylacetonates, intense bands are found in the region 1500—1700 cm^{-1}, corresponding to the C=O+C=C stretching bands in the spectra of $M(acac)_4$. Other bands are possibly a combination band of bands appearing in the 700—800 cm^{-1} region such as CH

Table 2. Frequencies of the intense bands in the 1500—1700 cm^{-1} (cm^{-1})

Metal	Ligand						
	acac	tfac	hfac	bzac	dbm	bfac	TTA
U(IV)	1577	1620	1643	1590	1590	1605	1618
		1600	1619	1562		1595	1600
	1525	1545	1568	1552	1542	1564	1570
		1530	1538	1525	1522	1535	1540
Th(IV)	1580	1620	1645	1589	1591	1605	1622
		1590	1620	1560		1595	1604
	1523	1545	1570	1551	1542	1565	1573
		1530	1543	1524	1520	1536	1544
Ce(IV)	1575	1618	1643	1587	1589	1606	1617
		1595	1620	1560		1595	1598
	1518	1545	1564	1545	1540	1564	1570
		1525	1535	1520	1520	1535	1542

Table 1. Infrared frequencies for $M(acac)_4$ chelates

$U(acac)_4$	$Th(acac)_4$	$Ce(acac)_4$	Predominant mode[a]
1577 vs[b]	1580 vs	1575 vs	$\nu(C{=}O)+\nu(C{=}C)$
1525 vs	1523 vs	1518 vs	$\nu(C{=}C)+\nu(C{=}O)$
1448 m	1448 m	1440 sh	$\delta d(CH_3)$
1390 vs	1390 vs	1386 vs	$\delta(C\text{–}H)+\nu(C{=}O)$
1365 sh	1365 sh	1365 sh	$\delta s(CH_3)$
1267 s	1267 s	1267 s	$\nu(C\text{–}CH_3)+\nu(C{=}C)$
	1199 vw	1198 vw	
1189 w	1192 w	1190 w	$\delta(CH)+\nu(C\text{–}CH_3)$
1019 s	1020 s	1020 s	$\rho r(CH_3)$
944 w	943 w	945 w	$\nu(C\text{–}CH_3)$
924 s	924 s	924 s	$\nu(C{=}C)+\nu(C{=}O)$
803 w	803 vw	803 vw	$\pi(CH)$
794 w	794 w	793 w	
779 w	780 w	779 w	
764 m	765 m	764 m	
656 s	657 s	658 m	$\delta(C\text{–}CH_3)+$ring
647 sh	650 sh	650 sh	$\pi(CH_3CCO)$
562 vw	561 vw	560 vw	ring
524 s	524 s	525 m	
	404 sh		
399 s	397 s	400 s	$\delta(C\text{–}CH_3)+\nu(M\text{–}O)$
221 s	225 m	250 m	$\nu(M\text{–}O)$

a) ν, stretching; δ, in-plane deformation; π, out-of-plane deformation; ρ r, rocking; s, symmetric; d, degenerated; ring, ring deformation; R. substituent.
b) v, very; s, strong; m, medium; w, weak; sh, shoulder.

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[9] J. Lecomte, *Discuss. Farad. Soc.*, **9**, 225 (1950).

[10] M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).

out-of-plane deformation bands[10] and/or the split $\text{C}\cdots\text{O}+\text{C}\cdots\text{C}$ stretching absorption bands as a result of the lowered symmetry induced by the asymmetrical ligands such as tfac, bzac, bfac, and TTA in the chelate. The frequencies of the intense bands in the 1500—1700 cm^{-1} are summarized in Table 2.

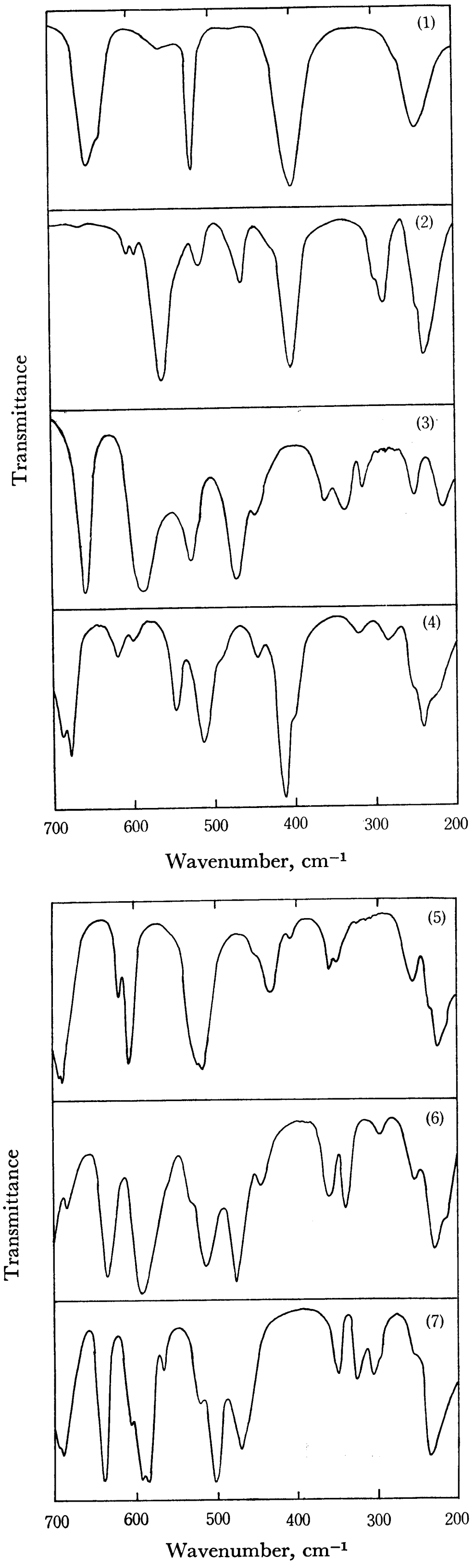

Fig. 2. Low-frequency infrared spectra of the tetrakis β-diketonates of Ce(IV).
(1) Ce(acac)$_4$, (2) Ce(tfac)$_4$, (3) Ce(hfac)$_4$, (4) Ce(bzac)$_4$, (5) Ce(dbm)$_4$, (6) Ce(bfac)$_4$, (7) Ce(TTA)$_4$.

In Fig. 2 are shown the IR spectra of the seven β-diketonates of Ce(IV) in the region 200—700 cm^{-1}. Vibrational bands contributed by appreciable amounts of M–O stretching mode are expected in the 500—200 cm^{-1} region. The spectra of M(acac)$_4$ show a strong band in the 220—250 cm^{-1} region and one in the 397—400 cm^{-1} region. The former band is relatively broad and metal sensitive, having a tendency to shift towards lower frequency side with an increase in the mass of the central metal, and can be assigned to the nearly pure M–O stretching mode, after the assignments for M(acac)$_4$ (M=Zr(IV), Hf(IV), Ce(IV), and Th(IV)) reported by Fay and Pinnavaia. The latter was assigned to a predominant M–O stretching mode.[3]

In tetrakis β-diketonates other than M(acac)$_4$, a strong, broad and metal sensitive band is found in the region 200—240 cm^{-1}. This band is also considered to be the nearly pure M–O stretching band corresponding to the 220—250 cm^{-1} band of M(acac)$_4$. The frequencies of the M–O stretching band in the lower frequency side are given in Table 3. They decrease for each metal ion in the order: M(acac)$_4$ > M(bzac)$_4$ > M(tfac)$_4$ > M(TTA)$_4$ > M(dbm)$_4$ > M(hfac)$_4$. In U(hfac)$_4$ and Th(hfac)$_4$ no such band was observed since it shifts out of the frequency region due to the mass effect of central metal ion.

Table 3. Frequencies of M–O stretching band (cm^{-1})

Metal	Ligand						
	acac	bzac	tfac	TTA	bfac	dbm	hfac
U(IV)	221	213	219	215	210	207	—
Th(IV)	225	215	212	212	210	210	—
Ce(IV)	250	242	240	233	230	225	218

In the β-diketonates containing the trifluoromethyl group, the M–O stretching band is found in the lower frequency side than that for M(acac)$_4$. This shows that the M–O bond is weakened because electron density on the carbonyl oxygens decreases by the strong electron-withdrawing property of the trifluoromethyl group. In the M(bzac)$_4$ and M(dbm)$_4$ which contain the phenyl group, the M–O stretching band is also found in the lower frequency side than that of M(acac)$_4$, showing that the M–O bond is weakened by the substitution of phenyl group for methyl group. This is in contradiction to the result reported by Nakamoto *et al.* in the study of the bis β-diketonates with Cu(II) and Ni(II), that the M–O bond is strengthened as a result of the mesomeric interactions of the phenyl group with the chelate ring.[6] The mesomeric interactions of the phenyl group with the chelate ring are assumed to occur only when the phenyl group is coplanar with the chelate ring. It has been suggested, however, by X-ray structure analysis for M(dbm)$_4$ (M=U(IV), Th(IV), and Ce(IV)) that the phenyl group is not coplanar with the chelate ring because of a steric hindrance.[8] The phenyl group seems hardly to release the electron by the mesomeric effect, but like the trifluoromethyl group, to act as an electron-withdrawing group by its inductive effect. Thus, in the β-diketonates with the phenyl group and probably with the 2-thienyl group, the M–O bond is weakened and the frequencies of the M–O stretching band are lowered as in the case of the trifluoromethyl group.

As the strength of the M–O bond changes with substituent, so is that of the C⋯O and C⋯C bonds expected to change. In fact, the C⋯O+C⋯C stretching bands move to the higher frequency side as the M–O stretching band moves to the lower. Thus, as the M–O bond weakens, the C⋯O and the C⋯C bonds are generally strengthened and their bands move to the higher frequency side. These tendencies are particularly remarkable in the β-diketonates with the trifluoromethyl group.