tween the various nonequivalent environments. Similar exchange for related eight-coordinate tetrakis diketonates has been reported previously.[24,33] In the case of *cis*-Ti(acac)$_2$X$_2$ complexes, this exchange is sufficiently slow so that separate resonance lines have been observed for nonequivalent methyl groups below −26 to −63°.[18] The zirconium and hafnium compounds, however, are considerably more labile. Spectra of Zr(acac)$_2$X$_2$ and Zr(acac)$_3$X (X = Cl and Br) at −108° in a mixture of dichloromethane and 1,1,2-trichloroethene (6:4 by volume) showed a single methyl resonance (line width, 1.4–1.8 cps). Spectra of Zr(acac)$_2$Cl$_2$, Zr(acac)$_3$Cl, and Zr(acac)$_4$ were also obtained at *ca.* −130° in dichloromethane–3-chloropropene (1:1 by volume); even at this low temperature only one rather sharp methyl resonance was observed (line width *ca.* 2–3 cps). Assuming that chemical shifts between nonequivalent protons are similar to that for Ti(acac)$_2$Cl$_2$,[18] rate constants for exchange of methyl groups can be estimated to be >10 sec^{-1} at −130.°

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Infrared and Raman Spectra of Some Six-, Seven-, and Eight-Coordinate Acetylacetonato Complexes of Zirconium(IV) and Hafnium(IV)[1]

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Infrared (4000–70 cm^{-1}) and Raman spectra are reported for six-coordinate dihalobis(acetylacetonato) and seven-coordinate halotris(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), M(acac)$_2$X$_2$ (X = Cl or Br) and M(acac)$_3$X (X = Cl, Br, or, when M = Zr, I). Spectra are also reported for the eight-coordinate acetylacetonato complexes, M(acac)$_4$ (M = Zr, Hf, Ce, or Th). Vibrational frequencies assigned to carbonyl stretching, metal–halogen stretching, and certain of the metal–oxygen stretching modes are sensitive to coordination number. The spectra indicate the *cis* configuration for the M(acac)$_2$X$_2$ complexes, and they afford confirmatory evidence for the seven-coordinate nature of the M(acac)$_3$X complexes.

Introduction

As a continuation of our study of the interesting six- and seven-coordinate halo(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), M(acac)$_2$X$_2$ and M(acac)$_3$X,[3] we have obtained infrared and Raman spectra of these compounds and the related eight-coordinate complexes, M(acac)$_4$ (M = Zr, Hf, Ce, or Th). The aim of this study was twofold. First, we hoped to identify the metal–oxygen and metal–halogen stretching vibrations. The M–O and M–X stretching region should afford additional evidence for the seven-coordinate nature of the monohalides and should provide a basis for distinguishing between the possible *cis* and *trans* structures for the dihalides. Second, these series of compounds offer an excellent opportunity to investigate the way in which the vibrational frequencies depend on coordination number.

Experimental Section

Preparation and characterization of the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes has been described in the preceding paper.[3] The tetrakisacetylacetonates were prepared by standard methods,[4-6] and the purity of these compounds was checked by their melting points.[4,7,8] Cerium(IV) acetylacetonate, which does not have a reproducible melting point, was satisfactorily analyzed.[9]

The starting materials used for preparation of all hafnium compounds were spectroscopic grade, <200 ppm zirconium; consequently, spectra of the hafnium compounds should be free of bands due to the zirconium analogs.

Infrared spectra in the 4000–250-cm^{-1} region were recorded using a Perkin-Elmer 521 grating spectrophotometer. The instrument was calibrated with reagent grade indene, freshly distilled from calcium hydride, and was swept with dry air while recording spectra. Solutions were contained in 0.1-mm cesium bromide cells; Nujol mulls were supported between cesium iodide plates. A fivefold frequency scale expansion was employed in the 600–250-cm^{-1} region. The maximum uncertainty in the reported frequencies is estimated to be less than 4 cm^{-1} and less than 2 cm^{-1} in the 1600–600- and 600–250-cm^{-1} regions, respectively.

Infrared spectra in the 322–70-cm^{-1} region were obtained with a Perkin-Elmer Model 301 grating spectrophotometer. This instrument was calibrated using the pure rotational bands of water vapor. Solution spectra were obtained in 0.1-mm polyethylene molded cells, and Nujol mulls were supported between polyethylene plates. The vapor of boiling nitrogen, after being warmed to room temperature, was used to purge the instrument while recording spectra. The estimated accuracy of reported frequencies in this region is ±2 cm^{-1}.

Raman spectra were obtained in nearly saturated benzene solutions using a Cary Model 81 Raman spectrophotometer. The spectra were excited with the 4358-Å mercury line; the 4047-Å line was removed with a Kodak Wratten 2A filter.

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[2] (a) Cornell University; (b) Michigan State University.

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TABLE I

VIBRATIONAL FREQUENCIES (CM^{-1}) FOR M(acac)$_2$X$_2$ COMPLEXES[a]

Zr(acac)$_2$Cl$_2$		Zr(acac)$_2$Br$_2$		Hf(acac)$_2$Cl$_2$		Hf(acac)$_2$Br$_2$		
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Predominant mode[b]
1575 vs[c]	*d*	1570	*d*	1579	*d*	1576	*d*	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1555 vs		1551		1556		1553		
1531 vs		1530		1534		1534		$\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1430 s		1428		1431		1431		CH$_3$ deg def
1361 sh	1370 s, p[c]	1360	1371	~1361	1372	~1361	1370	CH$_3$ sym def
1338 s		1333		1341		1337		$\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1287 s	1290 s, p	1287	1292	1287	1293	1287	1293	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1186 w	*d*	1183	*d*	1188	*d*	1186	*d*	δ(C—H)
1030 s		1028		1031		1031		CH$_3$ rock
953 w		951		~949 sh		~947 sh		ν(C—CH$_3$)
933 s		931		936		935		
798 m		798		801		802		π(C—H)
663 s	671 m, p	662	671	666	673	667	670	ν(M—O) + δ(C—CH$_3$) or δ (ring)
538 m		536		543		543		π(ring)?
460 sh	458 s, p	460	459	463 w	462	463 m	460	ν_s(M—O)
450 s	~450 sh	450	~450	446	~444	447	~445	ν_{as}(M—O)
410 m		410		411		411		π(ring)?
336[e] s	338 m, p	. . .		322[f] s 313[f] s	323 m, p	. . .		ν(M—Cl)
293 m		304 s	~301 m	264 m		266 s	268 w	ν(M—O)
. . .		286 s	285 m	252 m		252 s	~250 w	
263 w	260 w	248 m		. . .		. . .		
. . .		213 m	212 m, p	. . .		207 s	208 m, p	ν(M—Br)
179 w		~165 vw		177		168		Ring def

[a] Infrared frequencies above 320 cm^{-1} refer to dichloromethane solutions; concentrations: 9 g/100 ml (M = Zr) and 11 g/100 ml (M = Hf), except for the 1500–1600-cm^{-1} region where concentration was 2–5 g/100 ml. Infrared frequencies below 320 cm^{-1} and all Raman frequencies refer to benzene solutions; concentration, 9 g/100 ml. [b] ν_s, symmetric stretch; ν_{as}, asymmetric stretch; δ, in-plane deformation; π, out-of-plane deformation. [c] Relative intensities and polarization behavior also apply to other complexes unless indicated otherwise; v, very; s, strong; m, medium; w, weak; sp, sharp; b, broad; sh, shoulder; p, polarized; dp, depolarized. [d] This region obscured by solvent. [e] Doublet: 335, 325 cm^{-1} (Nujol mull). [f] Doublet: 318, 305 cm^{-1} (Nujol mull); singlet: 322 cm^{-1} (benzene solution).

TABLE II

VIBRATIONAL FREQUENCIES (CM^{-1}) FOR M(acac)$_3$X COMPLEXES[a]

Zr(acac)$_3$Cl		Zr(acac)$_3$Br		Zr(acac)$_3$I	Hf(acac)$_3$Cl		Hf(acac)$_3$Br		
Ir	Raman	Ir	Raman	Ir	Ir	Raman	Ir	Raman	Predominant mode[b]
1581 vs, sh[c]	*d*	~1580	*d*	. . .	1579	*d*	1574	*d*	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1568 vs	*d*	1566	*d*	1562	1570	*d*	1565	*d*	
1532 vs		1534		1533	1533		1532		$\nu_{as}(\mathrm{C}\cdots\mathrm{C})$
1428 s		1428		1429	1429		1430		CH$_3$ deg def
1381 s		1381		1380	1387		1386		$\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1360 s	1369 s, sp, p[c]	1362	1370	1360	1361	1370	1361	1370	CH$_3$ sym def
1283 s	1292 vs, sp, p	1283	1292	1285	1287	1293	1287	1291	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1186 w	*d*	1185	*d*	1185	1188	*d*	1188	*d*	δ(C—H)
1028 s	~1028[e] w	1027		1028	1029	~1030[e]	1029		CH$_3$ rock
947 sh	~945[e] w	948		947	~950	~950[e]	~950		ν(C—CH$_3$)
934 m		934		934	937		938		
788 m		788		790	790		791		π(C—H)
660 m	668 m, p	660	670	662	663	671 m, b, p	663	673 m, b, p	ν(*M*—O) + δ(C—CH$_3$) or δ (ring)
563 w	~560 w	561		563	564	564	563		π(ring)?
540 m		540		541	542		543		
449 sh	448 s, sp, p	449	449	452	454	452	454 w	452	ν_s(M—O)
432 s	431 sh	434	~430	438	432	433	433	~430	ν_{as}(M—O)
314 s		. . .		. . .	293	~296 vw	. . .		ν(M—Cl)
314 s		314		314	262	~258 vw	262		ν(M—O)
. . .		298 s		296 s	250 s, sh		249 s, sh		
~263 sh		262		~260	243 s, sh				
. . .		164 w		. . .	. . .		166 m		ν(M—Br)
. . .		. . .		93[f] w	. . .		. . .		ν(M—I)

[a,b,c,d] These notes are the same as in Table I except that the concentration of solutions for Raman spectra was *ca.* 30 g/100 ml. [e] Frequency somewhat uncertain due to partial solvent interference. [f] Nujol mull.

Calibration of the frequency scale was checked using the 606- and 1178-cm^{-1} benzene lines; reported frequencies for the strong, sharp lines should be accurate to ±3 cm^{-1}. Polaroid cylinders, which surrounded the Raman tube, were employed in order to identify the state of polarization of the Raman lines.

The tetrakisacetylacetonates gave colorless solutions and yielded excellent Raman spectra. Solutions of the monohalides and dihalides were slightly yellow,[10] and consequently only the stronger Raman lines could be observed. Solutions of Zr(acac)$_3$I were appreciably yellow; in this case, no Raman scattering could be detected.

Results

Infrared and Raman frequencies for the M(acac)$_2$X$_2$, M(acac)$_3$X, and M(acac)$_4$ complexes are listed in Tables I, II, and III, respectively. The infrared frequencies below 320 cm^{-1} and all Raman frequencies

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[10] Although the color increased with time, due to thermal and/or photochemical decomposition, solutions of the pure compounds are probably slightly yellow since the color could not be completely removed either by repeated recrystallization of the solids or by treatment of the solutions with dry, activated carbon.

Table III

Vibrational Frequencies (cm^{-1}) for M(acac)$_4$ Complexes[a]

Zr(acac)$_4$		Hf(acac)$_4$		Ce(acac)$_4$	Th(acac)$_4$		
Ir	Raman	Ir	Raman	Ir	Ir	Raman	Predominant mode[b]
1591 vs[c]	*d*	1592	*d*	1577	1581	*d*	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1524 vs	1528 w	1529	1528	1517	1521		$\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
~1450 sh		~1450		1437	1446		CH_3 deg def
1397		1397		1390	1395		$\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1367 s	1366 s, sp, p[c]	1366	1367	1362	1363	1364	CH_3 sym def
1279 s	1281 vs, sp, p	1277	1283	1267	1267	1271	$\nu_s(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1188 m	*d*	1187	*d*	1187	1188	*d*	δ(C—H)
1024 s	~1027[e] m	1025	~1026[e]	1020	1019	~1021[e]	CH_3 rock
~949 sh	~945[e] m	~947	~948[e]	943 m	942 m	~944[e]	ν(C—CH_3)
933 s		933		924	924		
767 s	772 w	775	771	770	771		π(C—H)
			670 m, p				
d	661 m, b, p	~655[e] s	660 sh, p	647[e] s	646[e] s	656 m, p	ν(M—O) + δ(C—CH_3) or δ (ring)
564 w	563 m, sp, dp	567	564	560	560	562	π(ring)?
538 m	535 w	541	537	523	523	~520	
. . .	441 s, sp, p	. . .	446	. . .	. . .	424	ν_s(M—O)
					406 sh		
421 s	416 m, b	422	417 m, dp	400	398	397 m, dp	ν_{as}(M—O)
301 s	~300 w, b	267 sh	~277	252	222		ν_{as}(M—O)
277 sh		253 s		~239		~242 w, b	
251 sh		233 s	~240 w, b				

[a] Infrared and Raman frequencies refer to benzene solutions; concentration, 9 g/100 ml for infrared spectra except for the 1500–1600-cm^{-1} region where concentration was *ca.* 1 g/100 ml; concentration, *ca.* 25 g/100 ml for Raman spectra. [b,c,d] These notes are the same as in Table I. [e] Frequency somewhat uncertain owing to partial solvent interference.

were measured using benzene solutions. Above 320 cm^{-1}, the infrared frequencies for the dihalides and monohalides (Tables I and II) refer to dichloromethane solutions; those for the M(acac)$_4$ complexes (Table III) refer to benzene solutions. The infrared spectrum of Hf(acac)$_4$ in the region 4000–250 cm^{-1} was obtained in both benzene and dichloromethane, and vibrational frequencies in the two solvents were found to agree within ±2 cm^{-1}.

With the exception of carbon–hydrogen stretching bands near 3000 cm^{-1}, no infrared bands were found above 1600 cm^{-1}. The C–H stretching bands are not of interest in the present work, and their frequencies have been excluded from the tables. In all cases, the 3000–3500-cm^{-1} region was carefully examined in order to verify that no water or hydroxyl groups were present.

For most of the complexes, infrared spectra of the solids were also recorded using the Nujol mull technique. In general, bands in the mull spectra above 250 cm^{-1} were only slightly shifted in frequency relative to the solution spectra. One prominent exception was the C–H out-of-plane bending mode near 790 cm^{-1}; in mulls, this band was split by 5–30 cm^{-1} into a doublet or triplet. Evidently in the solids the CH protons occupy two or more nonequivalent sites. The low-frequency regions of the infrared spectra are presented in Figures 1–3.

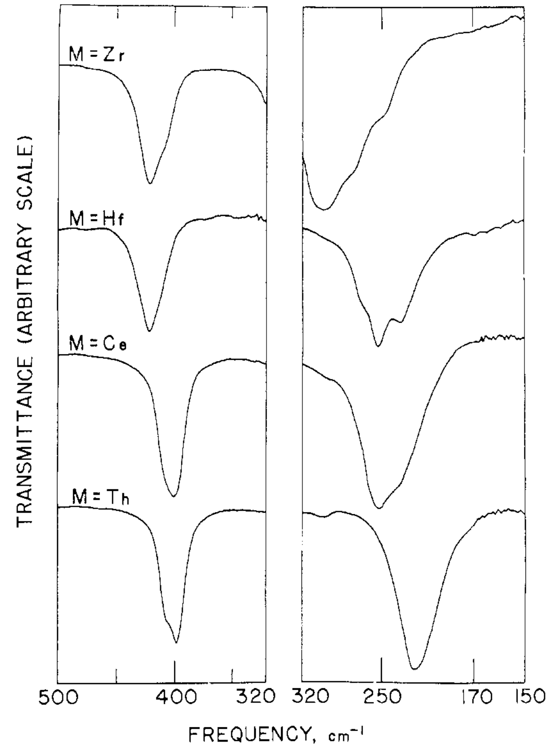

Figure 1.—Low-frequency infrared spectra of M(acac)$_4$ complexes in benzene solution.

Discussion

Infrared spectra of metal acetylacetonates have been studied by many investigators. The most complete band assignments have been based on normal coordinate treatments,[11–15] and in some cases these assignments have been substantiated by studies of deuterium isotope shifts[14,15] and infrared dichroism.[15] Raman spectra have been less extensively investigated; however, Raman studies have been reported for a few acetylacetonate complexes.[16–19]

Assignments. 1600–500-Cm^{-1} Region.—Assignments given in this paper for the 1600–500-cm^{-1}

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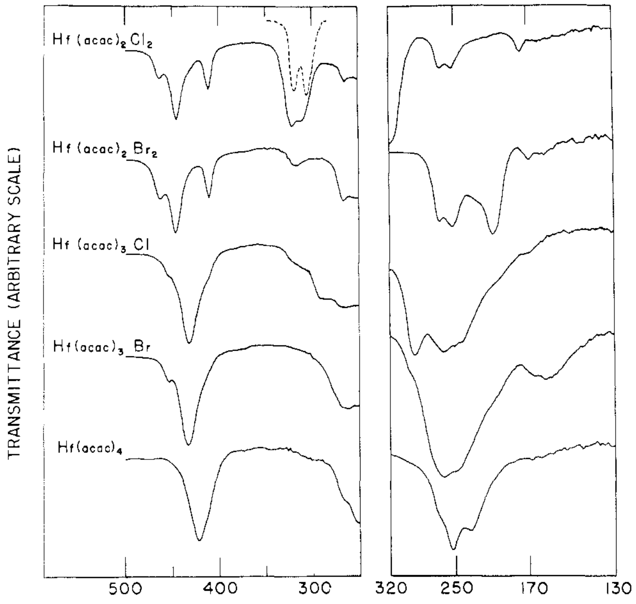

Figure 2.—Low-frequency infrared spectra of $Hf(acac)_2X_2$, $Hf(acac)_3X$, and $Hf(acac)_4$ complexes in solution; the solvent is benzene except for the 500–250-cm^{-1} region (left panel) of $Hf(acac)_2X_2$ and $Hf(acac)_3X$ spectra where the solvent is dichloromethane. The broken line gives the spectrum of solid $Hf(acac)_2Cl_2$ in a Nujol mull.

region (Tables I–III) are based on those reported by Behnke and Nakamoto in their recent study of $Pt(acac)Cl_2^-$, $Pt(acac)_2$, and the corresponding deuterated analogs.[14]

Infrared spectra of the $M(acac)_2X_2$, $M(acac)_3X$, and $M(acac)_4$ complexes in the chelating carbonyl stretching region (1300–1600 cm^{-1}) are generally similar to spectra of other metal acetylacetonate chelates.[12,13] No bands were observed in the 1600–1750-cm^{-1} region where ketonic carbonyl modes have been reported for the keto form of acetylacetone[20] and γ-carbon-bonded acetylacetonates of platinum(II).[21–24] Therefore, all carbonyl groups are coordinated. Chelation by all acetylacetonate ligands, together with the results of molecular weight and conductance experiments,[3] implies that the $M(acac)_2X_2$, $M(acac)_3X$, and $M(acac)_4$ complexes are, respectively, six-, seven-, and eight-coordinate in solution. The seven-coordinate nature of the monohalides is further confirmed by observation of metal–halogen stretching frequencies (see below).

The data in Table III show that vibrational frequencies for the $M(acac)_4$ complexes in the 1600–500-cm^{-1} region vary only slightly with changing mass of the metal. Little mass dependence is consistent with assignment of these vibrations to modes which involve primarily motion of the ligand atoms.

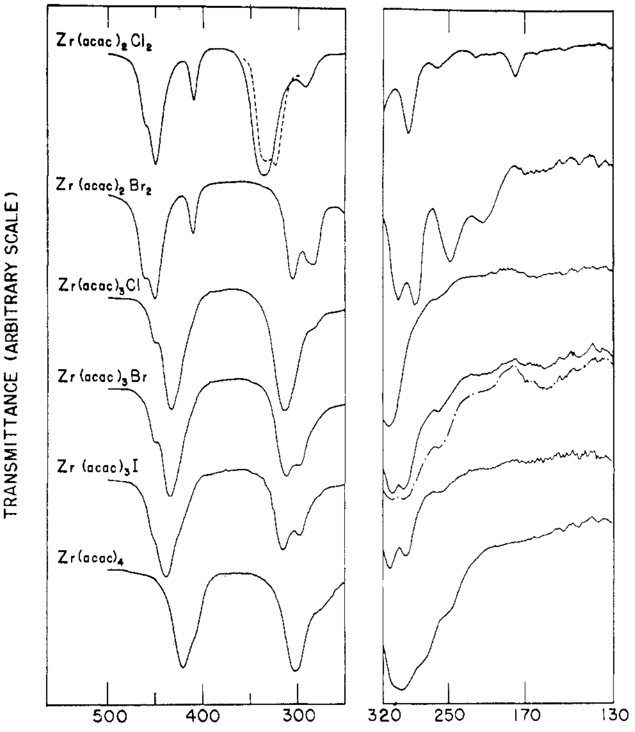

Figure 3.—Low-frequency infrared spectra of $Zr(acac)_2X_2$, $Zr(acac)_3X$, and $Zr(acac)_4$ complexes in solution; the solvent is benzene except for the 500–250-cm^{-1} region (left panel) of $Zr(acac)_2X_2$ and $Zr(acac)_3X$ spectra where the solvent is dichloromethane. The broken line gives the spectrum of solid $Zr(acac)_2Cl_2$ in a Nujol mull, and the dot-dash line gives the spectrum of $Zr(acac)_3Br$ in a more concentrated benzene solution (20 g/100 ml).

Comparison of the data in Tables I–III indicates that, with few exceptions, vibrational frequencies in the 1600–500-cm^{-1} region are nearly independent of the coordination number of the metal. The most prominent exception is the lower frequency carbonyl stretching band (due to asymmetric stretching in a C_{2v} one-ring model[14]), which shifts from *ca.* 1337 to 1383 to 1397 cm^{-1} as the coordination number increases from six to seven to eight. Carbonyl stretching vibrations in the 1550–1600-cm^{-1} region show parallel but less dramatic shifts to higher frequency with increasing coordination number. As the coordination number increases, one expects the metal–ligand bond distances to increase, thus decreasing the M–O bond strength and increasing the $C\overset{...}{=}O$ bond strength. The observed carbonyl frequency shifts are in accord with this expectation and will be seen to be paralleled by corresponding shifts in certain of the metal–oxygen stretching frequencies.

It is interesting to note that Nakamoto's earlier assignments[11–13] would identify the bands sensitive to coordination number as $C\overset{...}{=}C$ stretching and methyl degenerate deformation, whereas the more recent assignments[14] identify these bands with $C\overset{...}{=}O$ stretching. Thus, the more recent assignments are indirectly confirmed in the present work.

An additional feature of the carbonyl region which depends on coordination number is the number of bands between 1550 and 1600 cm^{-1}. The $M(acac)_4$ complexes show a single band; the monohalides, a

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band which has a high-frequency shoulder; and the dihalides, a clearly resolved doublet. The origin of this splitting is not clear, although it could result from coupling through the metal atom of the C$\overset{\cdots}{-}$O vibrations of different chelate rings.

The only other infrared band above 500 cm^{-1} which is appreciably sensitive to coordination number is the band assigned to C–H out-of-plane bending. This band appears at *ca.* 800, 790, and 770 cm^{-1}, respectively, in spectra of the six-, seven-, and eight-coordinate complexes.

The strongest lines in the Raman spectra are located near 1370 and 1290 cm^{-1}. These are assigned, respectively, to the symmetric methyl deformation and the symmetric C$\overset{\cdots}{-}$C stretching modes; consistent with this assignment, both lines are polarized.

500–70-Cm^{-1} Region.—This is the region in which one expects to observe vibrational modes involving appreciable amounts of metal–oxygen and metal–halogen stretching.

Assignment of Metal–Oxygen Stretching Modes.—Nakamoto and coworkers have demonstrated that a nearly pure M–O stretching band occurs in the 400–500-cm^{-1} region of infrared spectra of various metal acetylacetonates;[11–13] a metal-sensitive band in this region has also been reported by others.[15,25–28] A second M–O stretching frequency has been assigned to a very strong infrared band in the 200–400-cm^{-1} region.[15,27] The frequency of this band appears to be even more metal dependent than that of the 400–500-cm^{-1} band. Still another M–O stretching vibration, a totally symmetric, infrared-inactive mode, has been identified as a strong polarized line in the 400–500-cm^{-1} region of Raman spectra of certain metal acetylacetonates.[16,18]

Infrared spectra of the M(acac)$_4$ complexes (Figure 1 and Table III) reveal an intense band in the 398–422-cm^{-1} region and a second, very strong band in the 222–301-cm^{-1} region. The lower frequency band is broad, and, in some cases, it has one or two shoulders. Both of these bands, especially the lower frequency bands, are metal sensitive, generally shifting to lower frequency with increasing mass of the metal. In accord with previous assignments for other metal acetylacetonates, the 398–422- and 222–301-cm^{-1} bands are assigned to modes which are predominantly M–O stretching. Assuming that the eight-coordinate complexes have a square antiprismatic structure in solution,[29] these modes must be asymmetric (species B_1, B_2, or B_3 of the point group D_2) since the totally symmetric M–O stretching modes are infrared inactive.

In Raman spectra of the M(acac)$_4$ complexes (Table III) two lines are observed in the 400–500-cm^{-1} region. The 398–422-cm^{-1} M–O stretching vibration is seen as a depolarized line of medium intensity. A strong, sharp line is observed at 25–30 cm^{-1} above the depolarized line; the strong line, which is polarized and metal sensitive, is assigned to an infrared-inactive, totally symmetric M–O stretching mode.

Infrared and Raman spectra of the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes (Figures 2 and 3; Tables I and II) reveal M–O stretching modes in the same general region as found for the M(acac)$_4$ complexes. A totally symmetric mode appears in the 448–463-cm^{-1} region as a weak to medium intensity band (or shoulder) in the infrared spectra and as a strong, polarized line in the Raman spectra. An asymmetric M–O stretching mode is observed at slightly lower frequencies (430–450 cm^{-1}) with the reverse relative intensities, *i.e.*, very strong in the infrared but with only medium intensity in the Raman spectra. All of the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes exhibit two or three metal-sensitive infrared bands in the 243–314-cm^{-1} region, where we have earlier assigned broad absorption for the corresponding M(acac)$_4$ complexes to M–O stretching. Although some of these bands could be due to ring deformations, the stronger ones, at least, are tentatively assigned to M–O stretching. In any case none of the bands in the 243–314-cm^{-1} region, except the 293-cm^{-1} band of Hf(acac)$_3$Cl (see below), can be uniquely assigned to metal–halogen stretching, since the vibrational frequencies are relatively independent of the halogen.

Average frequencies for the M–O stretching vibrations are summarized in Table IV in order to show how the frequencies depend on coordination number. The bands in the lower energy range exhibit no obvious systematic trend, but the two 400–500-cm^{-1} bands clearly shift to lower frequency with increasing coordination number. As was mentioned earlier, this shift, which is paralleled by an increase in the carbonyl frequencies, can be rationalized in terms of the expected increase in the M–O bond distances as the coordination number changes from six to seven to eight.

Assignment of Metal–Halogen Stretching Modes.—Zirconium–halogen and hafnium–halogen stretching vibrations are expected in the region below 360 cm^{-1}. The infrared-active M–X stretching mode, $\nu_3(T_{1u})$, in MX$_6^{2-}$ anions has been observed at 293-295,[30–32] 273,[31] and $\lesssim$200 cm^{-1},[32] respectively, for ZrCl$_6^{2-}$, HfCl$_6^{2-}$, and ZrBr$_6^{2-}$. In spectra of metal tetrahalide addition compounds with various organic bases, M–X stretching frequencies have been assigned to bands in the regions 276–361 (Zr–Cl), 273-347 (Hf–Cl), and $\leq$270 cm^{-1} (Zr–Br).[33–36]

Comparison of the spectra in Figure 2 indicates

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TABLE IV

AVERAGE METAL–OXYGEN STRETCHING FREQUENCIES (CM^{-1})

Compound	ν_s(M–O)		ν_{as}(M–O)		ν(M–O)
	Ir	Raman	Ir	Raman	Ir (range)
$Zr(acac)_2X_2$[a]	460	459	450	~450	248–304
$Zr(acac)_3X$	450	449	435	~433	260–314
$Zr(acac)_4$	. . .	441	421	416	251–301
$Hf(acac)_2X_2$	463	461	447	~445	250–268
$Hf(acac)_3X$	454	452	433	432	243–262
$Hf(acac)_4$	. . .	446	422	417	233–267

[a] X = Cl and Br except for $Zr(acac)_3X$ where X = Cl, Br, and I.

that assignment of hafnium–halogen stretching modes in the halo(acetylacetonato) complexes is relatively unambiguous. The dichloride gives a strong band centered at 322 cm^{-1} in benzene solution (doublet at 322 and 313 cm^{-1} in dichloromethane solution; doublet at 318 and 305 cm^{-1} in Nujol mull) which is not present in the spectrum of the dibromide. The dibromide shows a unique, strong band at 207 cm^{-1}. The 322 and 207-cm^{-1} bands are assigned, respectively, to the Hf–Cl and Hf–Br stretching modes of $Hf(acac)_2X_2$; these modes appear in the Raman spectra as polarized lines of medium intensity.

Similarly, unique bands at 293 and 166 cm^{-1} in spectra of the monohalides (Figure 2) may be assigned, respectively, to the Hf–Cl and Hf–Br stretching modes of $Hf(acac)_3X$. In the Raman spectrum of $Hf(acac)_3Cl$ a very weak band is observed at *ca.* 296 cm^{-1} (intensity *ca.* 30 times less than that of the ν_s(M–O) band at 452 cm^{-1}); however, we have been unable to detect a line due to M-X stretching in Raman spectra of the other $M(acac)_3X$ complexes.

The Zr–X stretching modes should occur at frequencies which are similar to, though perhaps slightly larger than, those found for the Hf–X modes. The intense infrared band at 336 cm^{-1} in the solution spectrum of $Zr(acac)_2Cl_2$ (*cf.* Figure 3) is assigned to the Zr–Cl stretching modes; in mull spectra of the solid, this band is split into a doublet (335 and 325 cm^{-1}), and in the Raman spectrum it appears as a polarized line at 338 cm^{-1}. The dibromozirconium compound exhibits medium-intensity infrared bands at 248 and 213 cm^{-1}. Two reasons are cited for assigning the latter rather than the former band to Zr–Br stretching. First, like M–X stretching vibrations of the other $M(acac)_2X_2$ complexes, the 213-cm^{-1} vibration gives a polarized line in the Raman spectrum; however, the 248-cm^{-1} vibration is not observed in the Raman spectrum. Second, the ratio ν(Hf–Br)/ν(Zr–Br) coincides with the ratio ν(Hf–X)/ν(Zr–X) characteristic of the other $M(acac)_2X_2$ and $M(acac)_3X$ complexes for the 213-, but not for the 248-cm^{-1} assignment. The 248-cm^{-1} band is tentatively identified with the band near 260 cm^{-1} in spectra of the other zirconium complexes, but its greater intensity is not understood.

The Zr–Cl stretching frequency in $Zr(acac)_3Cl$ is expected below ν(Zr–Cl) of $Zr(acac)_2Cl_2$ (336 cm^{-1}) but above ν(Hf–Cl) of $Hf(acac)_3Cl$ (293 cm^{-1}). Only one band is present in this region (Figure 3), a very strong band at 314 cm^{-1}, previously assigned to a Zr–O stretching mode. It must be assumed in this case that the Zr–O and Zr–Cl frequencies are nearly coincident. The Zr–Br stretching vibration in $Zr(acac)_3Br$ gives a weak band at 164 cm^{-1}, but, because of the limited solubility of $Zr(acac)_3I$, the corresponding Zr–I stretching mode is not observed in solution spectra. However, a weak band is clearly present at 93 cm^{-1} in the Nujol mull spectrum of the solid monoiodide. This band is not present in mull spectra of $Zr(acac)_3Cl$ or $Zr(acac)_3Br$, and it is therefore tentatively assigned to the Zr–I stretching mode.

The metal–halogen stretching frequencies are summarized in Table V. It is apparent that frequencies for analogous zirconium and hafnium complexes are very similar; ν(Hf–X)/ν(Zr–X) = 0.97 ± 0.03. The ratio of ν(M–X) for the seven-coordinate complexes to ν(M–X) for the six-coordinate complexes is 0.92 ± 0.01 for X = Cl and 0.79 ± 0.02 for X = Br. Thus, the metal–halogen stretching force constant decreases with increasing coordination number (presumably owing to an increase in the M–X bond length[34]), and the decrease is greater in the case of the bulkier halogen. It is interesting to note that metal–chlorine stretching frequencies for the eight-coordinate adducts of zirconium(IV) chloride and hafnium(IV) chloride with *o*-phenylenebisdimethylarsine,[34] $MCl_4 \cdot 2diars$, are even lower than those for the seven-coordinate $M(acac)_3Cl$ complexes. The ratio ν(M–Br)/ν(M–Cl) found in this work is 0.64 ± 0.01 for the six-coordinate dihalides and 0.55 ± 0.03 for the seven-coordinate monohalides.

TABLE V

METAL–HALOGEN STRETCHING FREQUENCIES[a]

Stretching mode	Compound	
	$M(acac)_2X_2$	$M(acac)_3X$
Zr–Cl	336[b]	314
Hf–Cl	322	293
Zr–Br	213	164
Hf–Br	207	166
Zr–I	. . .	93[c]

[a] Frequencies (cm^{-1}) refer to benzene solutions unless indicated otherwise. [b] Dichloromethane solution. [c] Nujol mull.

In the foregoing discussion, several features of the infrared spectra have been mentioned which distinguish the six- and seven-coordinate complexes, *viz.*, the frequency and resolution of the carbonyl stretching bands and the frequency of the M–O and M–X stretching bands. An equally striking difference (*cf.* Figures 2 and 3) is the characteristic, sharp band of medium intensity at 410 cm^{-1} in spectra of the dihalides, which is completely absent in spectra of the monohalides.

Stereochemistry.—The possible *cis* and *trans* structures for $M(acac)_2X_2$ complexes can be distinguished on the basis of their different infrared and Raman selection rules. All vibrational modes of the *cis* isomer (point group C_2) are allowed in both infrared and Raman spectra, but, for the centrosymmetric *trans* isomer, infrared-active modes are Raman inactive, and *vice versa.* The coincidence of bands in the infrared and Raman spectra (Table I), especially those in the low-frequency region which have been assigned to M–O and M–X stretching modes, indicates that the $M(acac)_2X_2$ complexes exist in solution as the *cis* isomer. The *cis* structure was suggested for the zirconium and hafnium complexes by nmr chemical shift data,[3] and this stereochemistry has been well established for the analogous titanium[37,38] and tin[19,39–41] compounds.

Infrared and Raman spectra of the *cis* isomers should show two M–X stretching vibrations—a symmetric, Raman-polarized mode and an asymmetric mode. In spectra of the $M(acac)_2X_2$ complexes the single, rather broad M–X stretching band is generally not resolved. Only in infrared spectra of the solid dichlorides and of $Hf(acac)_2Cl_2$ in dichloromethane were two M–X bands observed, and even in these cases the frequency separation between the symmetric and asymmetric components was only *ca.* 10 cm^{-1}. Similar small-frequency separations and lack of resolution have been reported in infrared studies of other *cis*-dihalometal acetylacetonates.[14,19,36,37]

Infrared and Raman spectra afford no clue to the stereochemistry of the seven-coordinate $M(acac)_3X$ complexes because of the low symmetry of the possible geometrical isomers.

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Electron-Transfer Rate Studies of a Number of Cobalt(II)–Cobalt(III) Systems

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The kinetics have been studied of the oxidation of $Co(terpy)_2^{2+}$ by a series of cobalt(III) oxidants, $Co(bipy)_n(H_2O)_{6-2n}^{3+}$ and $Co(phen)_n(H_2O)_{6-2n}^{3+}$, $n = 0$–3, as well as the reaction of $Co(py)_4Cl_2^+$ with a series of cobalt(II) reductants, $Co(phen)_3^{2+}$, $Co(bipy)_3^{2+}$, and $Co(terpy)_2^{2+}$. The effect of (a) free energy drive, (b) aquo compared with hydroxo species, and (c) electronic configuration on the rates of these outer-sphere reactions could therefore be assessed. The reaction rate constant for the redox reaction between $Cr(bipy)_3^{2+}$ and $Cr(terpy)_2^{3+}$ exceeded $3 \times 10^6\ M^{-1}\ sec^{-1}$.

Introduction

Outer-sphere redox reactions do not involve bond cleavage during electron transfer and attention has been mainly focused on these types of reactions by the theoreticians.[1] In the present work we have investigated the kinetics of oxidation of a common reductant, $Co(terpy)_2^{2+}$, by a series of cobalt(III) oxidants, $Co(bipy)_n(H_2O)_{6-2n}^{3+}$ and $Co(phen)_n(H_2O)_{6-2n}^{3+}$, $n = 0$–3, as well as $Co(tmp)_3^{3+}$, tmp = 3,5,6,8-tetramethyl-1,10-phenanthroline. We have also studied the reaction of a common oxidant, $Co(py)_4Cl_2^+$, by a series of cobalt(II) reductants, $Co(phen)_3^{2+}$, $Co(bipy)_3^{2+}$, and $Co(terpy)_2^{2+}$. This allows us to examine in a systematic way the effect of (a) free energy drive, (b) the relative reactivity of aquo and hydroxo species, and (c) electronic configuration, specifically low- and high-spin cobalt(II), on the rates of outer-sphere reactions. These systems were chosen because we have useful information on the kinetics of isotopic exchange[2] among $Co(phen)_3^{2+}$–$Co(phen)_3^{3+}$, $Co(bipy)_3^{2+}$–$Co(bipy)_3^{3+}$, and Co $(terpy)_2^{2+}$–$Co(terpy)_2^{3+}$ and the lability in neutral and acid media of the cobalt (II) complexes,[3] both important for interpretive purposes.

Experimental Section

Materials.—Crude 2,2′-bipyridine was a gift from Imperial Chemical Industries Ltd., through the courtesy of Dr. A. Jubb. It was purified by heating *in vacuo* at 130° and recrystallizing the sublimate from absolute ethanol. Other chemicals used were commercial products. A number of solid complexes were prepared by literature methods and characterized by their spectra. These included (references refer to preparation and spectra, respectively) $Co(bipy)_3(ClO_4)_3 \cdot 3H_2O$,[4,5] $Co(phen)_3(ClO_4)_3 \cdot 2H_2O$,[2,6] $Co(terpy)_2(ClO_4)_3 \cdot H_2O$,[2,7] *cis*- and *trans*-$Co(bipy)_2Cl_3 \cdot$

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