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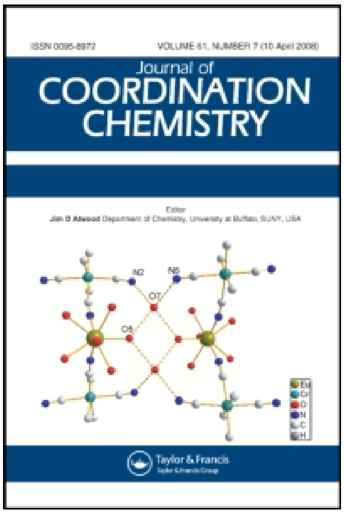

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Sergio Sitran[a]; Dolores Fregona[a]; Giuseppina Faraglia[b]
[a] Istituto di Chimica e Tecnologia dei Radioekmenti del C.N.R., Padora, Italy [b] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Universitá, Padova, Italy

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MIXED ACETATO-DEHYDROACETATO COMPLEXES OF LANTHANIDES

SERGIO SITRAN,* DOLORES FREGONA

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020, Padova, Italy,

and GIUSEPPINA FARAGLIA

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan 4, 35100 Padova, Italy.

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By reaction of hydrated lanthanide(III) acetates and dehydroacetic acid, H(Dh), in anhydrous methanol at the appropriate molar ratio, the complexes $[Ln(Dh)_2(O_2CMe)(L)_n]$ ($L = H_2O$, $n = 2$; $L = MeOH$, $n = 1$) have been obtained. Mixtures of both water and methanol solvates have been isolated. The influence of solution water content on complex purity is discussed. The complexes have been characterized by infrared and nmr (^1H and ^{13}C) spectroscopy and by thermogravimetric measurements. The nmr spectra are of help in determining the best conditions for the substitution of the acetato groups by dehydroacetato anions.

Keywords: Lanthanides, acetate, dehydroacetate, mixed complexes, nmr

INTRODUCTION

As a part of a research programme on *f*-block metal complexes with Schiff base condensation precursors,[1-3] we reported recently lanthanide(III) complexes of 3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one (H(Dh), dehydroacetic acid).[4] By reaction of lanthanide triacetate and ligand at a molar ratio of 1:3 in methanol, the species $[Ln(Dh)_3(L)]$ (Ln = Ce, Pr, Nd, Sm, Eu or Gd; $L = H_2O$ or MeOH) were isolated, except for lanthanum, which under the same conditions formed the mixed complex $[La(Dh)_2(O_2CMe)]$. Moreover, slow evaporation of the 1:3 complex mother solutions sometimes yielded solid fractions which seemed to contain mixed acetato-dehydroacetato species, as suggested by proton nmr spectra. Because dehydroacetic acid is a weak acid, whose strength in water ($pK_a = 5.26$)[5] is comparable to that of acetic acid, the substitution of the acetato group in lanthanide salts is critical. Proton nmr signals are strongly influenced by either lanthanide paramagnetism or complex geometry and so it was thought worthwhile to examine the lanthanide triacetate-H(Dh) system at various molar ratios. Accordingly, this paper reports the synthesis and characterization of mixed complexes containing the $[Ln(Dh)_2(O_2CMe)]$ group.

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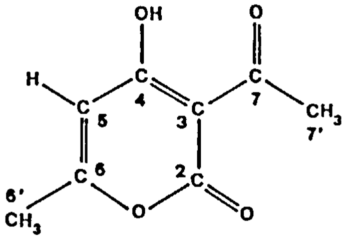
* Author for correspondence.



EXPERIMENTAL

Chemicals

Dehydroacetic acid, H(Dh), was a Fluka product. Hydrated lanthanide triacetates (J. Matthey) were used as supplied. Water content in each sample was estimated by thermal analysis. In complex preparations anhydrous methanol was generally used.

Preparation of the Compounds

The complex $[La(Dh)_2(O_2CMe)]$ was prepared as reported in ref. 4. The complex $[Ce(Dh)_2(O_2CMe)(MeOH)]$ was prepared by dissolving $Ce(O_2CMe)_3.1.5H_2O$ (1.0 mmol) and H(Dh) (2.0 mmol) in anhydrous methanol (25 cm^3). The yellow solution separated on standing (6 d) yellow crystals, which were filtered and washed twice with diethylether and *n*-pentane and dried *in vacuo*. Yield, 70%. Under identical conditions the reaction of $Nd(O_2CMe)_3.1.0H_2O$ and H(Dh) gave the species $[Nd(Dh)_2(O_2CMe)(H_2O)(MeOH)_{0.5}]$ whereas the reaction of $Pr(O_2CMe)_3.1.2H_2O$ and ligand yielded a mixture of $[Pr(Dh)_3(H_2O)]$ and $[Pr(Dh)_2(O_2CMe)(H_2O)_2]$. The latter complex was obtained by reacting praseodymium triacetate and H(Dh) in a 1:1 molar ratio. The pale-green solution separated within one week green crystals of the product, which were filtered and washed with *n*-pentane. Yield, 35%. The soluton obtained by mixing $Sm(O_2CMe)_3.1.8H_2O$ (0.82 mmol) and H(Dh) (1.64 mmol) in methanol (15 cm^3) did not separate any solid on standing for several days. It was then evaporated to a small volume (2 cm^3) under nitrogen flux to yield beige crystals suspended in an oily residue. The mixture was treated twice with methanol/diethylether (1:1 in volume). The $[Sm(Dh)_2(O_2CMe)(H_2O)_2]$ crystals were filtered and washed with *n*-pentane. Yield, 40%. Crystalline samples of $[Ln(Dh)_2(O_2CMe)(H_2O)_2]$ (Ln = Eu or Gd) separated (2–4 d) from a methanol solution (5 cm^3) of $Eu(O_2CMe)_3.3.8H_2O$ (or $Gd(O_2CMe)_3.4.0H_2O$), (0.6 mmol) and H(Dh) (1.2 mmol). The white solids were decanted and washed quickly with a small amount of chilled methanol and then with *n*-pentane. Yield, 40%. The analogous terbium or dysprosium complexes were obtained by slow evaporation under nitrogen flux of methanol solutions containing hydrated triacetate (1.0 mmol) and ligand (3.0 mmol in 25 cm^3) to incipient precipitation. Addition of diethylether under vigorous stirring (2–3 h) yielded white powders, which were filtered and washed with *n*-pentane. Yield, 50%.

The species $[Ln(Dh)_2(O_2CMe)]$ were obtained by heating the related solvates in the thermoanalysis apparatus up to the appropriate desolvation temperature.

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Measurements

Infrared spectra (4000–400 cm^{-1}; KBr pellets) were obtained by using a Perkin Elmer 580B spectrophotometer. Nmr (^{1}H and ^{13}C) spectra were obtained with a Jeol FX 90 Q spectrometer. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 cm^3 min^{-1}; reference material Al_2O_3).

RESULTS AND DISCUSSION

The nature of the species obtained by reaction of lanthanide triacetates with dehydroacetic acid in methanol depends on either the stoichiometric ratio of reagents or the water content of solutions. When anhydrous lanthanide salts and ligand were reacted in methanol at a molar ratio of 1:3, the species [Ln(Dh)$_3$(MeOH)] were obtained, except for lanthanum, which formed the unsolvated, mixed complex [La(Dh)$_2$(O$_2$CMe)]. By operating under identical conditions at molar ratio 1 : 2, the products were essentially solvated 1:2 mixed species made impure by 1:3 complexes. Pure samples of the 1:2 complexes (Table I) have been prepared from hydrated lanthanide acetates and ligand (molar ratio 1:2) in anhydrous methanol, except for the praseodymium derivative, which has been obtained using a molar ratio of 1: 1.Moreover, terbium and dysprosium triacetates also gave 1 : 2 complexes in the presence of a ligand excess. When the reaction solutions contained larger amounts of hot water they were evaporated in air, mixtures of 1:2 and 1:1 species were obtained, identified in most cases by the different nmr signals of the acetato protons.

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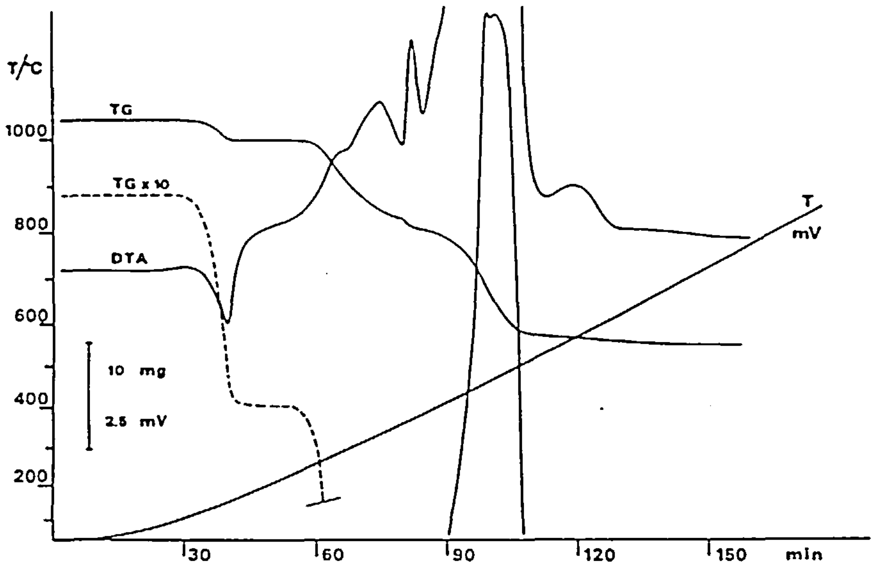

FIGURE 1 Thermograms of [Gd(Dh)$_2$(O$_2$CMe)(H$_2$O)$_2$] (31.77 mg).

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TABLE I

Analytical and thermoanalytical data for the complexes (calculated values in parentheses).

Compound	colour	C%	H%	Decomposition interval	TG weight loss %		DTA peacks (°C)[a]
					Found	Calcd	
$[Ce(Dh)_2(O_2CMe)(MeOH)]$[b]	yellow	39.7	3.5	129–185	5.6	5.6 (−MeOH)	167(en)
		(40.3)	(3.7)	185–435	68.6	69.2[c]	190(ex), 290(sh), 404(ex)
$[Pr(Dh)_2(O_2CMe)(H_2O)]_2]$[d]	green	37.4	3.5	105–160	6.0	6.3 ($-2H_2O$)	145(en)
		(37.9)	(3.7)	230–675	67.6	68.1[e]	338(ex), 359(ex), 515(ex)
$[Nd(Dh)_2(O_2CMe)(H_2O)(MeOH)_{0.5}]$[f]	violet	38.2	3.3	103–182	2.7	3.1 ($-H_2O$)	136(en)
		(38.9)	(3.7)		2.6	2.7(−0.5 MeOH)	176(en)
				227–685	69.1	68.7[c]	330(ex), 349(ex), 449(ex)
$[Sm(Dh)_2(O_2CMe)(H_2O)_2]$[d]	beige	37.1	3.6	90–180	6.9	6.2 ($-2H_2O$)	133(en)
		(37.3)	(3.7)	240–675	68.3	67.9[c]	278(sh), 327(ex), 370(ex)
							433(ex), 461(sh)
$[Eu(Dh)_2(O_2CMe)(H_2O)_2]$[d]	white	37.0	3.7	90–165	6.7	6.2 ($-2H_2O$)	145(en)
		(37.2)	(3.6)	225–830	67.5	67.7[c]	308(ex), 417(ex), 456(ex)
$[Gd(Dh)_2(O_2CMe)(H_2O)_2]$[d]	white	36.6	3.6	103–155	6.2	6.1 ($-2H_2O$)	142(en)
		(36.8)	(3.6)	225–740	67.9	67.7[c]	324(ex), 362(ex), 460(ex), 560(sh)
$[Tb(Dh)_2(O_2CMe)(H_2O)_2]$[d]	white	37.0	3.5	90–160	6.4	6.1 ($-2H_2O$)	142(en)
		(36.7)	(3.6)	210–750	68.7	66.9[c]	354(ex), 430(ex), 466(ex)
$[Dy(Dh)_2(O_2CMe)(H_2O)_2]$[d]	white	36.1	3.7	90–165	6.8	6.1 ($-2H_2O$)	132(en)
		(36.5)	(3.6)	220–690	66.8	66.4[c]	272(sh), 343(ex), 443(sh), 499(ex)

[a] (ex), exotherm; (en), endotherm; (sh), shoulder. [b] $C_{19}H_{21}CeO_{11}$. [c] For M_2O_3 as final product. [d] $C_{18}H_{21}MO_{12}$. [e] For Pr_6O_{11} as final product. [f] $C_{18.5}H_{21}NdO_{11.5}$.

Although the mixed complexes contain generally two water molecules, they sometimes have been isolated as either methanol or water–methanol solvates. The nature of the solvated molecules has been determined by combined nmr and thermogravimetric data. Thermograms of the dihydrated complexes resemble those of $[Gd(Dh)_2(O_2CMe)(H_2O)_2]$ (Figure 1), in which the first degradation refers to evolution of both water molecules, the related endotherm being observed at 142°C. The anhydrous mixed species begin to decompose at 225°C in successive exothermic steps. In all dihydrated species the release of water molecules occurs in the 130–145°C temperature interval, whereas in methanol adducts the solvent is evolved at higher temperatures (160–180°C), as previously observed for the $[Ln(Dh)_3(MeOH)]$ complexes. When the mixed complexes contain either water or methanol, as for $[Nd(Dh)_2(O_2CMe)(H_2O)(MeOH)_{0.5}]$ (Table I), the thermograms show in the 130–190°C range two successive endothermic processes, the one at lower temperature being related to water evolution. Because degradation of the anhydrous mixed species starts well beyond the desolvation temperature, they are easily obtained by heating the parent solvates directly in the thermobalance crucible up to the end of the desolvation endotherms.

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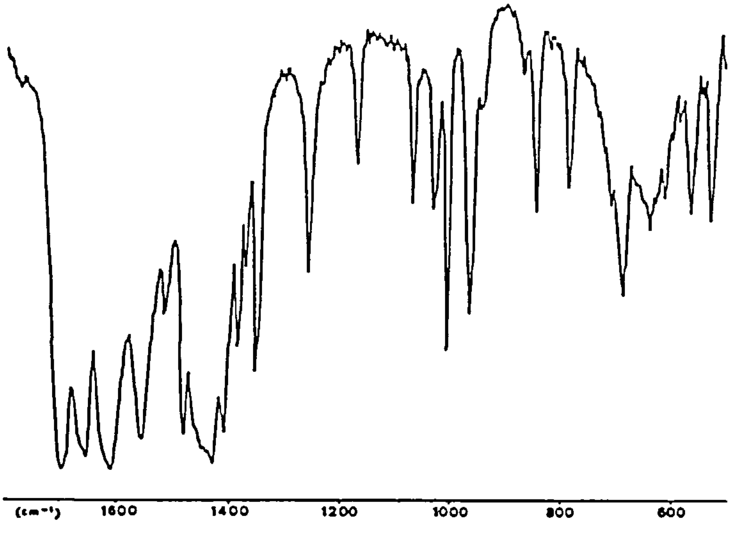

FIGURE 2 Infrared spectrum of $[Gd(Dh)_2(O_2CMe)(H_2O)_2]$.

Infrared spectra of the mixed species present a number of bands in the 1700–1400 cm^{-1} range, mainly due to the dehydroacetato ligand. For example, the $[Gd(Dh)_2(O_2CMe)(H_2O)_2]$ spectrum (Figure 2) contains in this region four strong bands (cm^{-1}: 1705, 1661, 1617 and 1562) along with a weak absorption at 1515 cm^{-1}. By comparison with the $[Gd(Dh)_3(MeOH)]$ spectrum and on the basis of correlations with characteristic wavelengths of pyrone and acetyl groups,[6–9] the higher energy absorption should be assigned to ν(C=C) of the dehydroacetato ring whereas the chelated acetylphenolato group should cause the absorption at 1617 cm^{-1}. Owing to ligand geometry, the pyrone carbonyl is probably uncoordinated, at least in the solvated species, the corresponding ν(C=O) stretch being observed at 1661 cm^{-1}. The band at 1562 cm^{-1}, absent in the parent 1:3 complex spectrum, belongs to acetato group vibrations. Apart for small shifts, the spectra of the solvated complexes look like those of the gadolinium derivative in both band shape and intensity. In the anhydrous mixed species the strong dehydroacetato absorptions are observed at *ca* 1693, 1662 and 1600 cm^{-1}, whereas the acetato absorption weakens and appears as a shoulder on the nearby band at 1600 cm^{-1}. The presence of the acetato group is confirmed by a medium absorption at *ca* 693 and 680 cm^{-1} in the solvated and anhydrous species, respectively.

TABLE II
^1H-nmr data for the complexes (d_6-DMSO; ppm; T *ca* 27°C).

Compound	CH	$CH_{3\ acyl}$	$CH_{3\ ring}$	$CH_{3\ acetate}$	other
$[La(Dh)_2(O_2CMe)]$[a]	5.49	2.30	2.03	1.69	
$[Ce(Dh)_2(O_2CMe)(MeOH)]$	8.28	2.90	2.35	2.89[b]	3.18, 4.09[c]
$[Pr(Dh)_2(O_2CMe)(H_2O)_2]$	11.70	4.15	3.11	5.35	3.28[d]
$[Nd(Dh)_2(O_2CMe)(H_2O)(MeOH)_{0.5}]$	8.96	2.94	2.86	3.56	3.17, 4.08,[c] 3.31[d]
$[Sm(Dh)_2(O_2CMe)]$	6.22	2.63	2.27	1.88	
$[Eu(Dh)_2(O_2CMe)]$	3.34	1.68[e]	1.25[e]	−0.8	
H(Dh)[a]	6.26	2.54 sh	2.25 sh		16.49[f]

[a] From ref. 4. [b] Shoulder of the CH_3(acyl) singlet. [c] MeOH protons. [d] H_2O protons. [e] Tentative assignment. [f] OH proton.

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The proton nmr spectrum of H(Dh) contains two close singlets at 2.54 ppm and 2.25 ppm assigned to protons of acyl methyl and ring methyl respectively, the ring CH resonance being observed at 6.26 ppm. The spectra have been measured in deuterated dimethyl sulphoxide (Table II) owing to the insolubility of lanthanide dehydroacetato derivatives in the usual nmr solvents. The dehydroacetato resonance trend in mixed complexes parallels that observed for the 1:3 complexes, the proton signal depending mainly on the metal magnetic properties. In general, paramagnetic effects overcome coordination effects in producing noticeable signal shifts. Major changes with respect to the free ligand concern the ring CH resonance, which is observed upfield in $[La(Dh)_2(O_2CMe)]$ (5.49 ppm) because of the lanthanum ion's diamagnetic properties. Conversely, this signal undergoes a noticeable downfield shift in the cerium (8.28 ppm), praseodymium (11.70 ppm) and neodymium (8.96 ppm) complexes, but is nearly unchanged (6.22 ppm) in the $[Sm(Dh)_2(O_2CMe)]$ spectrum. In the $[Eu(Dh)_2(O_2CMe)]$ spectrum all dehydroacetato signals are upfield with respect to H(Dh), the CH proton signal being observed at 3.34 ppm. The trend in the acetato proton resonances suggests an analogous dependence on the central ion, the larger opposite shifts being observed in the praseodymium (δ 5.35 ppm) and europium (δ −0.8 ppm) complexes. Except for cerium, the acetato proton singlet is well separated from the dehydroacetato resonances, allowing the complex purity to be assessed by integration. Moreover, proton nmr spectra in most cases detect the presence of unreacted lanthanide triacetate in successive fractions from complex syntheses. For example, the spectra of $[Pr(Dh)_2(O_2CMe)]$ samples containing praseodymium triacetate show a further acetato signal at *ca* 5.7 ppm, whereas for europium the analogous resonance is observed at *ca* −0.3 ppm. Since dimethyl sulphoxide is a stronger donor than either water or methanol towards lanthanide ions, the solvate molecules are removed from the metal coordination sphere and are clearly identified by proton nmr. In the spectra of several samples the free methanol signals seem to

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TABLE III

^{13}C-nmr data for the complexes (d_6-DMSO; ppm; T *ca* 27°C).[a]

Compound	C_7	C_4	C_6	C_2	C_5	C_3	$C_{7'}$	$C_{6'}$	$CO_{2\,\mathrm{acetato}}$	$CH_{3\,\mathrm{acetato}}$
$[La(Dh)_2(O_2CMe)]$[b]	196.6	180.3	162.3[c]	164.8[c]	107.4	103.3	31.5	19.3	181.8	24.7
$[Ce(Dh)_2(O_2CMe)(MeOH)]$[d]	204.2	193.7	164.1	168.0	117.7	115.3	[e]	21.2	173.8	33.6
$[Pr(Dh)_2(O_2CMe)]$	217.3	216.1	169.3	172.2	134.4	129.8	47.2	23.9	154.5	52.4
$[Nd(Dh)_2(O_2CMe)]$	210.1	199.9	166.5	166.2	133.1	116.4	48.7	22.4	127.4	59.1
$[Sm(Dh)_2(O_2CMe)]$	200.0	184.8	163.7	165.4	106.3	104.1	30.6	19.5	187.2	23.3
$[Eu(Dh)_2(O_2CMe)]$	189.7	166.3br[c]	156.6	160.1br[c]	78.0	63.1br	3.7	15.1	[f]	−41.2
$H(Dh)$[b]	204.5	180.3	170.1	160.3	100.9	99.3	29.6	20.0		

[a] Numbering scheme in the figure. [b] From ref. 4. [c] Tentative assignment. [d] MeOH carbon, 48.6 ppm. [e] at *ca* 39 ppm, obscured by solvent multiplet. [f] Not observed.

increase slowly to the maximum value for a fully released molecule, thus suggesting a slow methanol–dimethyl sulphoxide exchange, whereas water–dimethyl sulphoxide exchange is immediate.

In accordance with the assignments reported in ref. 10, the carbon nmr spectrum of H(Dh) contains the acyl C=O and phenolato carbon signals at 204.5 ppm and 180.3 ppm respectively, whereas the resonances at 100.9 ppm and 99.3 ppm belong to the ring carbons bearing hydrogen and the acetyl group, respectively (Table III). These signals are the more affected by lanthanide coordination, the larger downfield shifts, of the order of 25–30 ppm, being observed for [Pr(Dh)$_2$(O$_2$CMe)]. The fact that the lactone carbonyl group does not coordinate to the lanthanide ion, at least in dimethyl sulphoxide solution, is supported by the smaller shift of the related carbonyl signal. As is shown in Figure 3, the [Sm(Dh)$_2$(O$_2$CMe)] spectrum presents well resolved signals, the weak ones at 187.2 and 23.3 ppm belonging to the acetato CO$_2$ and CH$_3$ carbons, respectively. In the Ce, Pr and Nd analogues the acetato CO$_2$ resonance appears progressively upfield, an opposite downfield shift being observed for the acetato methyl signal. As regards the dehydroacetato fragment, the carbon spectrum of [Eu(Dh)$_2$(O$_2$CMe)] shows broad unresolved resonances upfield with respect to H(Dh), whereas the acetato methyl carbon gives a broad signal at −41.2 ppm.

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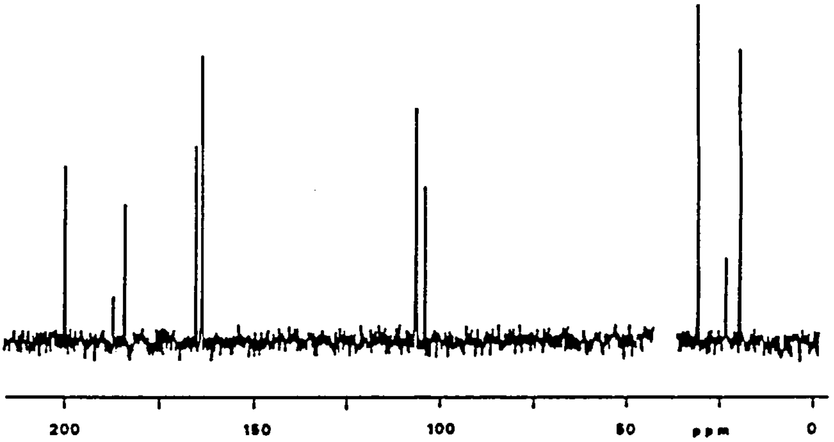

FIGURE 3 ^{13}C nmr spectrum of [Sm(Dh)$_2$(O$_2$CMe)] with proton decoupling (solvent d_6-DMSO).

The proton nmr spectrum of the gadolinium complex is uninterpretable because of excessive broadening. The spectra of terbium and dysprosium analogues contain very broad signals well downfield with respect to H(Dh). In fact, the proton nmr spectrum of [Tb(Dh)$_2$(O$_2$CMe)] shows the ring CH resonance at *ca* 24 ppm, along with two methyl signals (approximately three protons from integration) at *ca* 22.5 ppm and 16.5 ppm. All resonances shift downfield and partially superimpose in the dysprosium mixed complex.

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