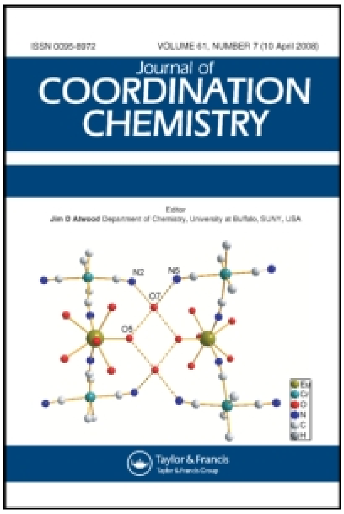

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Sitran, Sergio , Fregona, Dolores and Faraglia, Giuseppina(1990) 'Lanthanide Complexes of 3-Acetyl-4-Hydroxy-6-Methyl-2H-Pyran-2-One', Journal of Coordination Chemistry, 22: 3, 229 — 235

To link to this Article: DOI: 10.1080/00958979009408219

URL: http://dx.doi.org/10.1080/00958979009408219

J. Coord. Chem. 1990, Vol. 22, pp. 229–235
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LANTHANIDE COMPLEXES OF 3-ACETYL-4-HYDROXY-6-METHYL-2H-PYRAN-2-ONE

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(Received May 31, 1990)

The title ligand (H(Dh), dehydroacetic acid) reacts with lanthanide(III) acetates in anhydrous methanol to form complexes of formula $[M(Dh)_3(MeOH)]$. When hydrated lanthanide acetates are used, hydrated compounds such as $[Ce(Dh)_3(H_2O)]$ or $[Eu(Dh)_3(H_2O)].H_2O$ are obtained. The reaction of lanthanum triacetate with H(Dh) yields the mixed complex $[La(Dh)_2(O_2CMe)]$, formation of the 1:3 complex also being unfavoured in the presence of a large ligand excess. The complexes have been characterized by infrared and nmr (^1H and ^{13}C) spectroscopy and by thermogravimetric measurements.

Keywords: 3-Acetyl-4-hydroxy-6-methyl-2H-pyran-2-one, lanthanides, complexes, synthesis, thermal behaviour.

INTRODUCTION

Coordination compounds of dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) have not been extensively studied. As regards lanthanide complexes, consecutive stability constants in water containing 20% ethanol were measured by the potentiometric method.[1] The complex stability was found to increase from lanthanum ($\log K_1 = 4.18$; $\log K_2 = 3.26$; $\log K_3 = 2.91$) with metal mass, with a maximum for the erbium complexes ($\log K_1 = 4.86$; $\log K_2 = 3.72$; $\log K_3 = 3.45$). Moreover, the formation of mixed complexes with dehydroacetic acid and either ethylenediaminetetraacetic acid or nitrilotriacetic acid was followed by electronic spectra.[2,3] Dehydroacetic acid is a weak acid ($pK_a = 5.26$ in water) in which the 4-hydroxy group forms a strong intramolecular hydrogen bond with the acyl oxygen atom.[4] In reactions with primary amines, hydrazines or hydroxylamine, the initial condensation at the acyl oxygen can be followed either by ring opening or by formation of different heterocycles.[5,6] In previous studies of lanthanide and uranyl complexes with Schiff base condensation precursors we have examined the behaviour of lanthanide salts towards 2,6-diformyl-4-methylphenol and 2,6-dimethyl-4H-pyrone.[7,8] In this line the present paper reports a study of the interaction of dehydroacetic acid with lanthanide(III) acetates in methanol.

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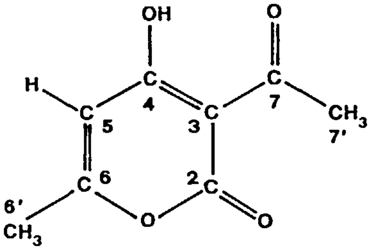

EXPERIMENTAL

Chemicals

Dehydroacetic acid [H(Dh), $C_8H_8O_4$, Fluka] was used as supplied. The water content in $Ln(O_2CMe)_3.nH_2O$ salts (J. Mattey) was determined by thermogravimetry (La, n = 1.0; Ce, 1.5; Pr, 1.2; Nd, 1.0; Sm, 1.8; Eu, 3.5; Gd, 4.0). Water molecules are totally released in the 50–180°C range.

Preparation of the Compounds

As a general method, the hydrated salt of the appropriate lanthanide was reacted with H(Dh) in anhydrous methanol at a molar ratio of 1 : 3. As an example, $[Pr(Dh)_3(MeOH)]$ was prepared by stirring a $Pr(O_2CMe)_3.1.2H_2O$ (1.1 mmol) suspension in a methanol solution of H(Dh) (3.3 mmol in 25 cm^3). The salt dissolved within 20 min to yield a greenish solution from which separated pale-green crystals of the complex overnight. The solid was filtered, washed with chilled methanol and *n*-pentane and dried *in vacuo*. Yield, 50%. Successive fractions obtained by slow evaporation of the mother solution under a nitrogen flux were progressively impure (mixed species containing acetato groups, which were easily detected by n.m.r.). In analogous conditions the complexes $[M(Dh)_3(MeOH)]$ (M = Nd or Sm) and $[Ce(Dh)_3(H_2O)]$ were isolated whereas for lanthanum the anhydrous mixed species $[La(Dh)_2(O_2CMe)]$ was obtained. Attempts to prepare the 1 : 3 lanthanum complex from anhydrous $La(O_2CMe)_3$ and H(Dh) at molar ratios up to 1 : 6 yielded species containing the acetato group and unreacted ligand. The reaction of $Eu(O_2CMe)_3.3.5\ H_2O$ (0.8 mmol) with H(Dh) (2.4 mmol) in methanol (10 cm^3) gave a colourless solution which by slow evaporation (to *ca* 5 cm^3) gave white crystals of $[Eu(Dh)_3(H_2O)].H_2O$ (yield, 20%). Further evaporation yielded mixtures containing the species $[Eu(Dh)_n(O_2CMe)_{3-n}]$ (n = 1 or 2). The complexes $[M(Dh)_3(MeOH)]$ (M = Eu or Gd) were prepared in good yield (70–80%), by adding H(Dh) (3.0 mmol) to the anhydrous triacetate (1.0 mmol) obtained by heating the hydrated salt under reduced pressure (170°C; oil bath; 3h). Anhydrous methanol was distilled over the reagents until complete dissolution was effected (5–8 cm^3). On standing under nitrogen (2d) the solution gave well shaped crystals, which were washed with dichloromethane and *n*-pentane and dried *in vacuo*. Further fractions of the product were obtained by evaporating the mother solution under a nitrogen flux.

Unsolvated samples of all complexes were obtained by heating the solvated species in the thermobalance crucible. Heating was stopped immediately after the end of the desolvation endotherm.

Measurements

Infrared spectra (4000–400 cm^{-1}; KBr pellets) were obtained with 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 complexes [M(Dh)$_3$(MeOH)] (Table I) have been prepared by reaction of anhydrous lanthanide triacetates with a stoichiometric amount of ligand in anhydrous methanol. In analogous conditions lanthanum triacetate yielded the mixed complex [La(Dh)$_2$(O$_2$CMe)]. Attempts to isolate the 1:3 lanthanum complex by using a large excess of dehydroacetic acid (up to 1:6) failed, the solid fractions being generally mixtures of the 1:2 mixed complex and ligand. Similar behaviour was observed for the reaction of lanthanum triacetate with 2,6-diformyl-4-methylphenol, H(MDA), the related products being either [La(MDA)$_2$(O$_2$CMe)] or [La(MDA)$_2$-(O$_2$CMe)].H(MDA). In the latter complex the neutral ligand molecule was easily released in solution or by gentle heating under reduced pressure. The formation of the unsolvated [La(Dh)$_2$(O$_2$CMe)] species could suggest that the primary reaction product is the unstable [La(Dh)$_2$(O$_2$CMe)].H(Dh) complex, the weakly bound H(Dh) molecule being extracted from the solid by washing with dichloromethane and *n*-pentane. When hydrated lanthanide salts were used in complex preparation, the 1:3 complexes of cerium, europium or gadolinium preferentially coordinated water, instead of methanol. Moreover, the presence of water was found to favour the formation of mixed acetato-dehydroacetato species, which are more soluble in methanol than the 1:3 dehydroacetato complexes. As an example, the species [Eu(Dh)$_2$(O$_2$CMe)] and [Eu(Dh)(O$_2$CMe)$_2$] have been identified by proton nmr spectra in successive fractions obtained by slow evaporation of the 1:3 complex mother solution.

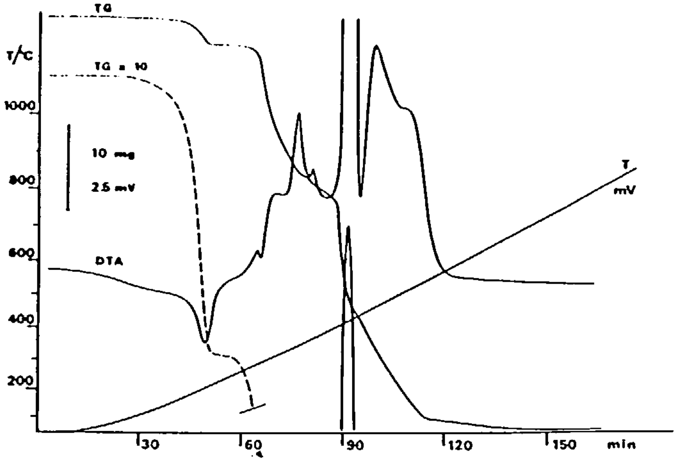

FIGURE 1 Thermograms of Eu(Dh)$_3$(MeOH) (64.47 mg).

TABLE I

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

Compound	Colour	C%	H%	Decomposition interval (°C)	TG weight loss % Found	TG weight loss % Calcd.	DTA peaks (°C)[a]
$[La(Dh)_2(O_2CMe)]$[b]	white	40.2	2.9	283–700	69.6	69.5[c]	311(ex), 465(ex), 540(sh)
		(40.6)	(3.2)				
$[Ce(Dh)_3(H_2O)]$[d]	yellow	43.9	3.5	85–166	2.8	2.7($-H_2O$)	150(en)
		(43.7)	(3.5)	258–450	72.6	72.4[c]	286(ex), 311(ex), 380(ex)
$[Pr(Dh)_3(MeOH)]$[e]	pale green	44.2	3.6	123–180	4.7	4.7(–MeOH)	164(en)
		(44.5)	(3.7)	241–590	70.7	70.1[f]	294(ex), 330(ex), 370(ex), 515(ex)
$[Nd(Dh)_3(MeOH)]$[e]	violet	44.0	3.7	106–176	5.1	4.7(–MeOH)	167(en)
		(44.3)	(3.7)	232–724	70.8	70.5[c]	295(ex), 327(ex), 370(ex), 492(ex)
$[Sm(Dh)_3(MeOH)]$[e]	beige	43.6	3.7	106–185	4.7	4.7(–MeOH)	164(en)
		(43.9)	(3.7)	236–696	71.2	69.8[c]	289(ex), 332(ex), 504(ex),
$[Eu(Dh)_3(H_2O)].H_2O$[g]	white	42.0	3.5	92–200	6.3	5.2($-2H_2O$)	103(en), 135(en)
		(41.8)	(3.6)	210–550	68.4	69.3[c]	283(ex), 310(ex), 495(ex)
$[Eu(Dh)_3(MeOH)]$[e]	white	43.7	3.6	113–206	5.0	4.7(–MeOH)	188(en)
		(43.8)	(3.7)	232–695	70.8	69.6[c]	266(ex), 291(sh), 327(ex), 345(ex), 407(ex), 443(ex)
$[Gd(Dh)_3(MeOH)]$[e]	white	43.7	3.8	161–197	4.6	4.6(–MeOH)	185(en)
		(43.5)	(3.7)	241–719	70.3	69.2[c]	266(ex), 294(sh), 358(ex), 422(ex), 479(ex), 567(sh)

[a] (ex), exotherm; (en), endotherm; (sh), shoulder. [b] $C_{18}H_{17}LaO_{10}$. [c] For M_2O_3 as final degradation product. [d] $C_{24}H_{23}CeO_{13}$. [e] $C_{25}H_{25}MO_{13}$. [f] For Pr_6O_{11} as final product. [g] $C_{24}H_{25}EuO_{14}$.

The thermal behaviour of the 1:3 adducts resembles that of $[Eu(Dh)_3(MeOH)]$ (Table I). As is shown in Figure 1, the methanol molecule is evolved at a relatively high temperature, the related endotherm being observed at 188°C (gadolinium complex, 185°C). In the analogous praseodymium, neodymium and samarium complexes desolvation takes place at slightly lower temperatures (164–167°C). The thermograms of $[Eu(Dh)_3(H_2O)].H_2O$ support a different bonding mode for the water molecules. In fact, water evolution occurs in two steps, the corresponding endotherms being at 103°C (outer sphere H_2O) and 135°C (coordinated H_2O). Some 1:3 complexes contain either water or methanol. In this case the thermograms show two successive desolvation steps, the one at lower temperature (120–150°C) being due to water evolution. As for the europium complex of Figure 1, the degradation of the anhydrous species occurs in exothermic steps, the first one corresponding to a 28–30% weight loss.

Because the infrared bands of H(Dh) in the 1750–1400 cm^{-1} region are due either to ring vibrations or to stretching of the carbonyl groups (acetyl and pyrone), the resolution of these highly mixed modes is difficult. The H(Dh) spectrum in nujol contains strong absorptions at 1720, 1643 (1618sh), 1551 and 1450 cm^{-1}. The spectra of the solvated and anhydrous 1:3 adducts are similar to that of $[Pr(Dh)_3(MeOH)]$, which shows two bands of medium intensity at 1728 and 1699 cm^{-1} along with strong broad absorptions at 1657, 1587 and 1425 cm^{-1}. The 2,6-dimethyl-4H-pyrone carbonyl absorption was observed at 1611 cm^{-1}, whereas ring vibrations should contribute to the bands at 1669, 1599 and 1444 cm^{-1}.[9] Moreover, the ν(C=O) mode of the hydrogen bridged acetyl group in 2-hydroxyacetophenone falls at 1580 cm^{-1}, the related absorption in chelated platinum or organoantimony complexes being observed at *ca* 1575 cm^{-1}.[10–12] Thus the high energy absorptions in the 1:3 complexes (at *ca* 1730 and 1690 cm^{-1}) should be assigned as ν(C=C), whereas the broad absorption at *ca* 1590 cm^{-1} should be due to the chelated acetylphenolato group. Owing to the chelated ligand geometry, coordination of the pyrone carbonyl should be unfavoured and the related ν(C=O) should contribute to the broad band at *ca* 1660 cm^{-1}. Accordingly, the spectrum of $[La(Dh)_2(O_2CMe)]$ contains the dehydroacetato bands at 1685, 1660 and 1600 cm^{-1}, along with the acetato carbonyl absorption at 1565 cm^{-1}. The presence of the acetato group is confirmed by a medium absorption at 675 cm^{-1}, common to the $[M(MDA)_2(O_2CMe)]$ (M = La or Ce) complexes.[7]

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

Compound	CH	$CH_{3\,ac}$	$CH_{3\,ring}$	Other
H(Dh)	6.26	2.54 sh	2.25 sh	16.49[a]
$[La(Dh)_2(O_2CMe)]$	5.49	2.30	2.03	1.69[b]
$[Ce(Dh)_3(H_2O)]$	7.99	2.85	2.43	3.28[c]
$[Pr(Dh)_3]$	11.47	4.17	2.98	
$[Pr(Dh)_3(MeOH)]$	11.36	4.04	2.97	3.16[d]
$[Nd(Dh)_3]$	8.90	3.05[e]	2.90[e]	
$[Nd(Dh)_3(MeOH)]$	8.85	3.02[e]	2.94[e]	3.19, 4.07[d]
$[Sm(Dh)_3(MeOH)]$	6.22	2.65	2.28	3.17, 4.09[d]
$[Eu(Dh)_3(MeOH)]$	3.40	1.25[e]	1.67[e]	3.17, 4.09[d]

[a] OH proton. [b] Acetato group protons. [c] H_2O protons. [d] MeOH protons. [e] Tentative assignment.

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	$C_{7'}$	$C_{6'}$	Other
H(Dh)	204.5	180.3	170.1	160.3	100.9	99.3	29.6	20.0	
[La(Dh)$_2$(O$_2$CMe)]	196.6	180.3	162.3[b]	164.8[b]	107.4	103.3	31.5	19.3	24.7, 181.8[c]
[Ce(Dh)$_3$(H$_2$O)]	204.0	193.2	164.1[b]	167.8[b]	117.4	115.3	[d]	21.1	
[Pr(Dh)$_3$]	216.0	214.0	168.7	171.4	133.5	129.6	46.5	23.6	
[Nd(Dh)$_3$]	210.5	199.7	166.6	166.2	133.1	117.7	48.7	22.3	
[Sm(Dh)$_3$(MeOH)]	200.3	184.2	163.8	165.4	106.3	104.2	30.7	19.4	48.6[e]
[Eu(Dh)$_3$(MeOH)]	190.5	166.2br[b]	156.5	160.8br[b]	77.8	63.1br	3.8	15.0	48.6[e]

[a] Numbering scheme in the figure. [b] Tentative assignment. [c] Acetato carbon atoms. [d] *Ca* 39.6, obscured by solvent signals. [e] MeOH carbon.

The signal positions in complex nmr spectra depend mainly on the different magnetic properties of the metal ions. The proton nmr spectrum of H(Dh) in deuterated dimethyl sulphoxide (Table II) shows the ring methyl singlet (2.25 ppm) upfield with respect to the acyl CH_3 group (2.54 ppm), the ring CH resonance being observed at 6.26 ppm. The presence of a strong intermolecular hydrogen bond, which stabilizes the enolic form, accounts for the strongly deshielded phenolic proton (16.67 ppm).[13] Owing to the diamagnetic effect of lanthanum,[7,8] dehydroacetato signals in [La(Dh)$_2$(O$_2$CMe)] are shifted upfield in respect to the corresponding H(Dh) resonances, the acetato proton singlet being observed at 1.69 ppm. Conversely, the well resolved singlets in the Ce, Pr and Nd spectra show a downfield shift, which depends on the combined influence of complexation and ion magnetism. As previously observed in the MDA complex series,[7] the downfield shift is at a maximum for [Pr(Dh)$_3$], the major change concerning the ring CH resonance (Δppm, *ca* 5.2). The shift is smaller in the neodymium complexes (ring CH Δppm, *ca* 2.6), whereas complexation and magnetism effects should balance in the samarium complex, whose resonances are close to those of H(Dh). An opposite shift is observed for the europium complex signals, the ring CH signal being 2.9 ppm upfield with respect to free ligand. Solvent exchange removes the MeOH molecule from the metal coordination sphere, as suggested by the common doublet (3.18 ppm) and quartet (4.08 ppm), the latter being obscured in the praseodymium adduct by the strong CH_3 (acyl) signal. On the basis of the assignments reported in ref. 13, the downfield signal in the H(Dh) ^{13}C nmr spectrum (Table III) belongs to the acyl C=O carbon (204.5 ppm), the phenolato carbon and lactone C=O resonances being observed at 180.3 and 160.3 ppm, respectively. The trend in ^{13}C nmr spectra of complexes resembles that observed in the proton nmr spectrum series. Lanthanide coordination affects mainly the phenolato carbon signal, along with the resonances of the nearby ring carbon atoms. As an example, in the praseodymium spectrum, the resonances of the ring carbons bound to either hydrogen or acetyl undergo a *ca* 30 ppm downfield shift, as does the phenolato carbon atom. As shown in Figure 2 for [Sm(Dh)$_3$], the carbon nmr spectra of the complexes generally contain well-resolved signals, whereas considerable broadening is observed for the europium complex resonances, which undergo more or less marked negative shifts. Chelation through the chain carbonyl influences the position of the acyl CH_3 resonance more than the ring methyl, the related ring carbon signal being upfield with respect to H(Dh). Shifts in the pyrone carbonyl resonance are smaller than for lanthanide nitrate adducts with 2,6-

dimethyl-4H-pyrone, suggesting that this group is not involved in coordination, at least in dimethyl sulphoxide solution. The presence of methanol in the solvated complexes is confirmed by the carbon signal at 48.6 ppm. The acetato carbons in [La(Dh)$_2$(O$_2$CMe)] cause the carbonyl and methyl carbon signals at 181.8 and 24.7 ppm, respectively.

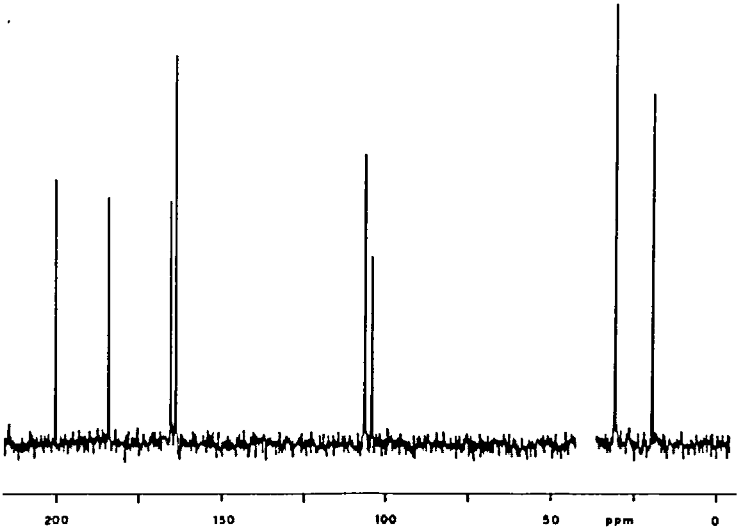

FIGURE 2 ^{13}C nmr spectrum of Sm(Dh)$_3$ with proton decoupling (solvent d_6-DMSO).

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