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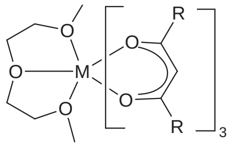
Yttrium β-diketonate complexes with triglyme: ionic and neutral isomers and outer-sphere co-ordination of triglyme †

Kimberly D. Pollard,[a] Jagadese J. Vittal,[a] Glenn P. A. Yap[b] and Richard J. Puddephatt *[,a]

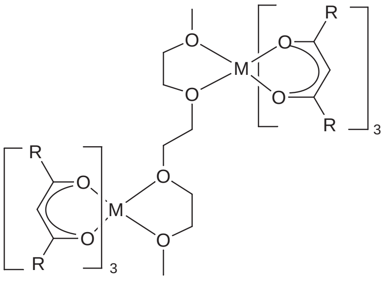
[a] *Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7*
[b] *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Canada N9B 3P4*

While monoglyme and diglyme reacted with [$Y^{III}(hfac)_3$] to give eight- and nine-co-ordinate neutral complexes [$Y(hfac)_3$(glyme)], **1** and **2** respectively, reactions with triglyme or tetraglyme resulted in disproportionation giving the ionic complexes [$Y(hfac)_2$(glyme)]$^+$[$Y(hfac)_4$]$^-$, **3a** and **4** respectively; sublimation of **3a** with adventitious water gave the outer-sphere glyme complex [$Y(hfac)_3(OH_2)_2$]·$MeO(CH_2CH_2O)_3Me$ which has an infinite chain helical structure.

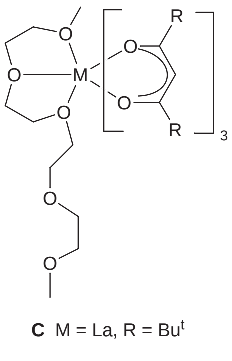
The β-diketonate derivatives of electropositive elements are important as volatile precursors for MOCVD of metal oxide ceramics, but the volatility can depend on the synthetic method and can change with time, due to effects such as self-association, hydrate formation, hydrolysis or cleavage of the β-diketonate ligands.[1–5] The formation of glyme complexes [$MeO(CH_2CH_2O)_nMe$; $n = 1$, monoglyme, L^1; $n = 2$, diglyme, L^2; $n = 3$, triglyme, L^3; *etc.*] can give co-ordinative saturation and hence improved stability with respect to self-association, hydrate formation and hydrolysis, while maintaining high volatility.[1–3] This approach has recently led to valuable new precursors for MOCVD of oxide ceramics containing lanthanides and yttrium and has also led to interesting new co-ordination chemistry of these elements.[1–5] Thus, while monoglyme and diglyme form mononuclear complexes [M(diketonate)$_3$(glyme)], such as **A**, the higher glymes can give bridged complexes [{M(diketonate)$_3$}$_2$(μ-glyme)], such as **B**, or complexes with some non-co-ordinated glyme oxygen donors, such as **C**.[1–3] This article shows that [$Y^{III}(hfac)_3$], can form new types of complexes with triglyme; the ionic complex [$Y(hfac)_2L^3$]$^+$-[$Y(hfac)_4$]$^-$ and the outer-sphere hydrate complex [$Y(hfac)_3(OH_2)_2$]·L^3, which has an interesting helical chain structure, have been characterized structurally.



A M = La or Gd, R = CF_3



B M = Y, R = Bu^t



C M = La, R = Bu^t

The new glyme complexes were prepared in yields of 50–70% by reaction of Y_2O_3 and Hhfac in refluxing benzene in the presence of glyme, and the products were recrystallized from hexane to give [$Y(hfac)_3L^1$] **1**, [$Y(hfac)_3L^2$] **2**, the ionic [$Y(hfac)_2L^3$][$Y(hfac)_4$] **3a** and, probably, [$Y(hfac)_2L^4$][$Y(hfac)_4$] **4**. Vacuum sublimation of **1** and **2** occurred easily but **3a** and **4** were less volatile and sublimation of **3a** gave an isomer **3b**, tentatively characterized as [{$Y(hfac)_3$}$_2$(μ-L^3)], **3b**. In most sublimations, the crystals of **3b** formed very thin needles which were unsuitable for X-ray structure determination but, on occasion, a few block-like crystals formed and one of these was characterized as an outer-sphere complex [$Y(hfac)_3(OH_2)_2$]·L^3, **5**; its formation clearly requires the presence of adventitious water during the sublimation. The triglyme complexes are shown in Scheme 1 and some physical properties of the complexes **1**–**4** are given in Table 1.

In $(CD_3)_2CO$ solutions the complexes **1**–**4** gave simple NMR spectra, with apparently equivalent hfac groups even at −80 °C, indicating very easy fluxionality; the spectra in CD_2Cl_2 are similar though resonances are broader and the solubility is low at −80 °C, thus hindering detailed studies of the fluxionality in a non-co-ordinating solvent. In addition, the spectra of **3a** and **3b** were identical, thus showing that they are isomers and interconvert very easily.‡

Complexes **2**, **3a** and **5** were characterized by X-ray structure determinations and the structures of **3a** and **5** are shown in Figs. 1 and 2.§ The structure of **2** is very similar to those of

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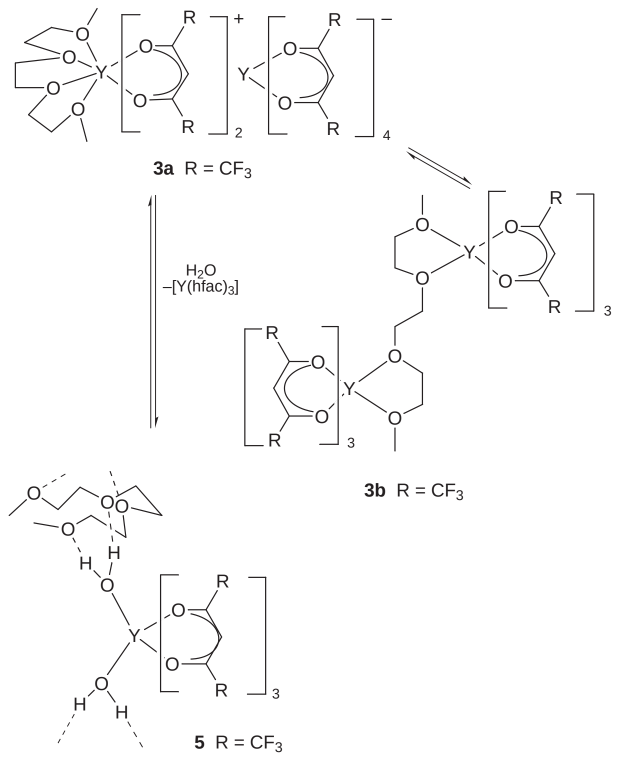
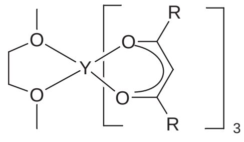
† Glyme compounds have the general formulae $MeO(CH_2CH_2O)_nMe$; $n = 1$, monoglyme; $n = 2$, diglyme; $n = 3$, triglyme or $n = 4$, tetraglyme; Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

‡ Selected NMR data [$(CD_3)_2CO$]: **1**, $\delta(^1H)$ 3.3 (s, 6 H, OCH_3), 3.4 (s, 4 H, OCH_2), 6.2 (s, 3 H, CH); $\delta(^{19}F)$ −76.1 (s, CF_3). **2**, $\delta(^1H)$ 3.3 (s, 6 H, OCH_3), 3.4 (m, 4 H, OCH_2), 3.5 (m, 4 H, OCH_2), 6.2 (m, 3 H, CH); $\delta(^{19}F)$ −76.6 (s, CF_3). **3a** or **3b**, $\delta(^1H)$ 3.3 (s, 6 H, OCH_3), 3.5 (m, 4 H, OCH_2), 3.6 (m, 8 H, OCH_2), 6.2 (s, 6 H, CH); $\delta(^{13}C)$ 58.7 (s, OCH_3), 71.1 (s, OCH_2), 71.3 (s, OCH_2), 72.7 (s, OCH_2), 91.2 (s, CH), 118.5 (q, $^1J_{C-F}$ 285, CF_3), 177.7 (q, $^2J_{C-F}$ 35 Hz, CO); $\delta(^{19}F)$ −76.7 (s, CF_3). **4**, $\delta(^1H)$ 3.3 (s, 6 H, OCH_3), 3.5 (m, 4 H, OCH_2), 3.6 (s, 12 H, OCH_2), 6.2 (s, 6 H, CH); $\delta(^{13}C)$ 58.9 (s, OCH_3), 71.1 (s, OCH_2), 71.4 (s, OCH_2), 72.0 (s, OCH_2), 91.2 (s, CH), 118.5 (q, $^1J_{C-F}$ 285, CF_3), 177.7 (q, $^2J_{C-F}$ 34 Hz, CO); $\delta(^{19}F)$ −76.8 (s, CF_3). Satisfactory C,H analyses were obtained for all new complexes.

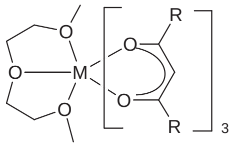
§ Crystal data: **2**, $C_{21}H_{17}F_{18}O_9Y$, $M = 844.26$, monoclinic, space group $P2_1/n$, $a = 10.202(2)$, $b = 16.225(2)$, $c = 19.192(2)$ Å, $\beta = 95.76(1)°$, $U = 3160.8(8)$ Å^3, $Z = 4$, $\mu = 1.996$ cm^{-1}, $T = 293(2)$ K, $R1 = 0.088$ for 1816 data with $I > 2\sigma(I)$; **3a**·$0.25C_6H_6$·$0.25C_6H_5CH_3$, $C_{41.25}H_{27.5}F_{36}O_{16}Y_2$, $M = 1640.95$, orthorhombic, space group $Fdd2$, $a = 38.5473(7)$, $b = 41.3150(2)$, $c = 15.6324(3)$ Å, $U = 24\,895.9(7)$ Å^3, $Z = 16$, $\mu = 2.022$ cm^{-1}, $T = 300(2)$ K, $R1 = 0.087$ for 8300 data with $I > 2\sigma(I)$; **5**, $C_{23}H_{25}F_{18}O_{12}Y$, $M = 924.34$, trigonal, space group P3(1)21, $a = 12.0579(2)$, $b = 12.0579(2)$, $c = 44.7674(9)$ Å, $U = 5636.8(2)$ Å^3, $Z = 6$, $\mu = 1.692$ cm^{-1}, $T = 296(2)$ K, R1 = 0.080 for 4022 data with $I > 2\sigma(I)$. CCDC reference number 186/926. See http://www.rsc.org/suppdata/dt/1998/1265/ for crystallographic files in .cif format.



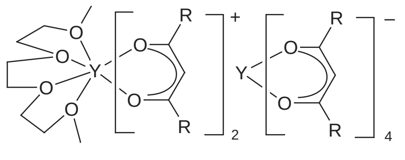
Scheme 1



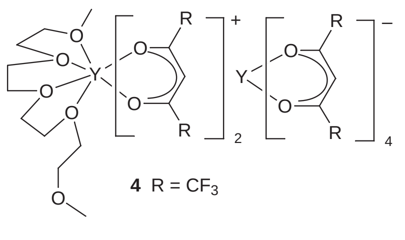
1 $R = CF_3$



2 $R = CF_3$



3a $R = CF_3$



4 $R = CF_3$

$[M(hfac)_3L^2]$ with M = Gd or La,[3] having nine-co-ordinate yttrium with approximately capped square antiprismatic stereochemistry, and is not shown.

Complex **3a** is shown to be $[Y(hfac)_2L^3]^+[Y(hfac)_4]^-$ (Fig. 1). The anion has been characterized previously as the caesium salt[6] but the cation is new and contains eight-co-ordinate yttrium bound to four oxygen atoms each from the triglyme and two hfac ligands. The formation of **3a** involves the unprecedented disproportionation of a β-diketonate complex by a glyme. It is noteworthy that **3a** melts and sublimes about 100 °C higher than the neutral glyme complexes **1** and **2** (Table 1). It also melts about 100 °C higher than complex **3b**, thus lending support to the characterization of **3b** as a neutral complex isostructural with **B**.[1] The high melting point and sublimation temperature of **4**, which are similar to those of **3a** (Table 1), suggest a similar ionic structure, perhaps with one of the oxygen atoms of tetraglyme not co-ordinated. Together, the data in Table 1 show a clear correlation between volatility and structure.

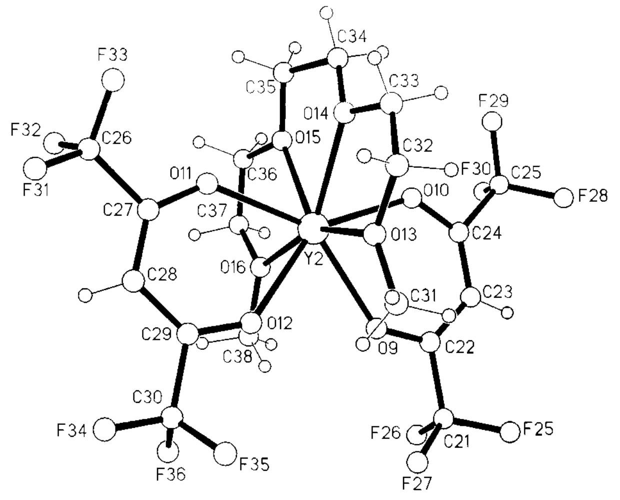


Fig. 1 A view of the structure of the cation $[Y(hfac)_2L^3]^+$. The stereochemistry is approximately dodecahedral, with Y2–O (hfac) from 2.283(7) to 2.322(6) Å and Y–O (glyme) from 2.323(7) to 2.385(7) Å

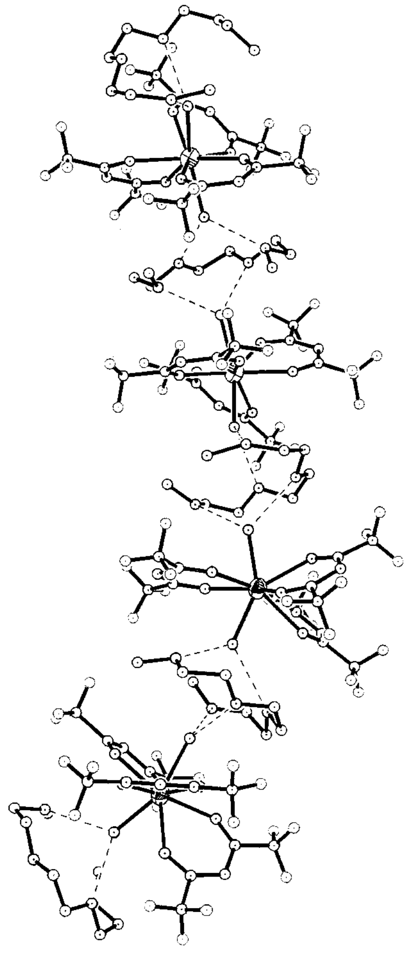


Fig. 2 A view of the helical chain structure $\{[Y(hfac)_3(OH_2)_2]\cdot L^3\}_n$. The dotted lines represent O–H · · · O hydrogen bonds and the O · · · O distances are in the range 2.76(1)–2.86(1) Å. The distances Y–O (hfac) and Y–O (H_2O) range from 2.316(8) to 2.381(9) and 2.335(7) to 2.336(8) Å respectively

Finally, complex **5** has a structure containing units of eight-co-ordinate $[Y(hfac)_3(OH_2)_2]$ with triglyme ligands in the outer co-ordination sphere hydrogen bonded to the aqua ligands. Each triglyme bridges two $[Y(hfac)_3(OH_2)_2]$ units by forming two hydrogen bonds to an aqua ligand of each, while each $[Y(hfac)_3(OH_2)_2]$ unit similarly bridges between two glyme ligands. As a result, an interesting infinite helical chain structure is built up, a segment of which is shown in Fig. 2.

Table 1 Melting points and sublimation temperatures of the complexes **1**–**4**

Complex	M.p./ °C	Sublimation temperature*/°C
1	54–56	40–60
2	81–83	65–85
3a	177–179	150–170
3b	69–72	60–70
4	181–183	165–185

* Complexes sublimed at 0.02 mmHg (1 mmHg = 133.322 Pa).

In conclusion, this work describes the first characterization of isomers, the establishment of disproportionation to ionic complexes, and the possibility of outer-sphere co-ordination in glyme complexes of yttrium β-diketonates. It deepens our understanding of the factors influencing volatility of these complexes, which can be important as CVD precursors. These complexes give mixed yttrium oxide–fluoride ceramics on CVD at 250–350 °C using oxygen as a carrier gas, with the hfac ligands acting as the source of fluoride.¶

Acknowledgements

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¶ X-Ray photoelectron spectroscopic characterization: binding energy of Y($3d_{\frac{5}{2}}$) peak = 158.4 eV (eV ≈ 1.602×10^{-19} J), intermediate between those of the pure oxide (156.4–157 eV) and fluoride (159.8 eV) phases. The O : F ratio varied from 6 : 1 to 1 : 2 depending on the precursor and the CVD conditions.