Synthesis and Crystal and Molecular Structure of Tris(*NN*-di-iso-propylcarbamato)ytterbium(III), $Yb_4(O_2CNPr^i_2)_{12}$–Heptane (1/2), the First Dialkylcarbamato Complex of a 4*f* Element

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Summary The reaction of anhydrous $YbCl_3$ with secondary amines and CO_2 in hydrocarbon solvents gave the *NN*-dialkylcarbamato complexes of ytterbium, $Yb(O_2CNR_2)_3$ ($R = Et$ or Pr^i); the di-isopropyl derivative is tetrameric with ytterbium heptaco-ordinated to three different types of carbamato groups.

The known examples of binary dialkylcarbamato complexes of transition elements are limited to uranium(IV),[1] zirconium(IV), vanadium(IV), niobium(V), tantalum(V),[2] titanium(IV),[3] and tungsten(III).[4] The niobium(V) and tungsten(III) complexes have been studied crystallographically. These complexes are usually prepared from the preformed dialkylamido complexes.

We report here an extension of our new method of preparation of uranium(IV) dialkylcarbamato derivatives to ytterbium(III). The dialkylcarbamato complexes of ytterbium(III) were obtained by the reaction of anhydrous $YbCl_3$ with an appropriate secondary amine and CO_2 in a hydrocarbon solvent according to equation (1).

$$YbCl_3 + 6\,NHR_2 + 3\,CO_2 \rightarrow Yb(O_2CNR_2)_3 + 3\,NH_2R_2{}^+Cl^- \quad (1)$$

The crystal and molecular structure of the isopropyl derivative was investigated using X-ray diffraction methods.

Crystal data: M 2622·9 [including lattice heptane for tetrameric $Yb_4(O_2CNPr^i_2)_{12}$–heptane (1/2)†], monoclinic, space group $C2/c$, $a = 29{\cdot}069(5)$, $b = 19{\cdot}591(3)$, $c = 23{\cdot}193(4)$ Å, $\beta = 107{\cdot}70(2)°$, $U = 12582{\cdot}9$ Å^3, $D_c = 1{\cdot}384$ g cm^{-3}, CuK_α radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = ca.$ 58 cm^{-1}, $Z = 4$. The structure was solved by Patterson and Fourier methods. At this stage of the refinement the R value is 0·13.‡

Intensities were collected with an automated Siemens AED diffractometer and Ni-filtered CuK_α radiation using the θ—2θ scan method. 7897 reflections were collected; 3368 had $I > 4.0\sigma(I)$ [$\sigma^2(I)$ = total counts + $(0.005\ I)^2$] and were used for structure solution.

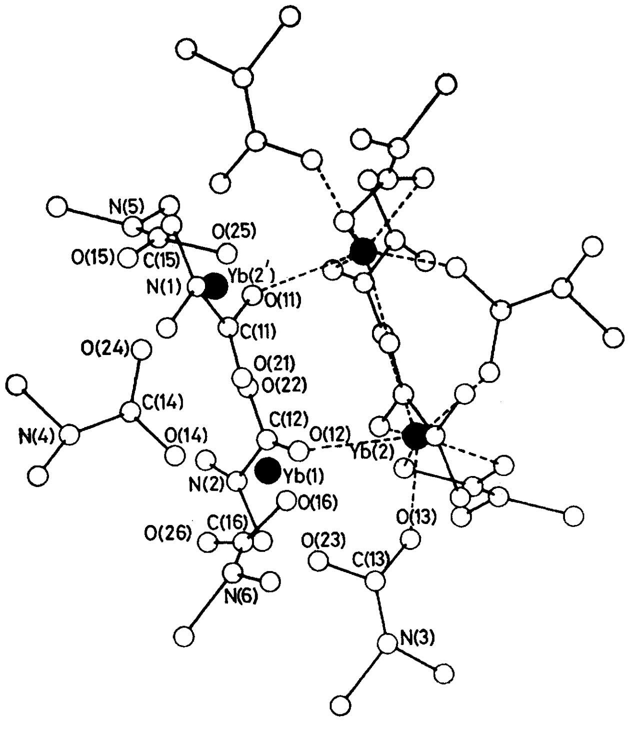
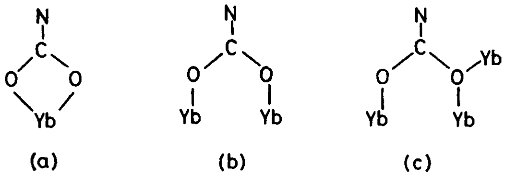
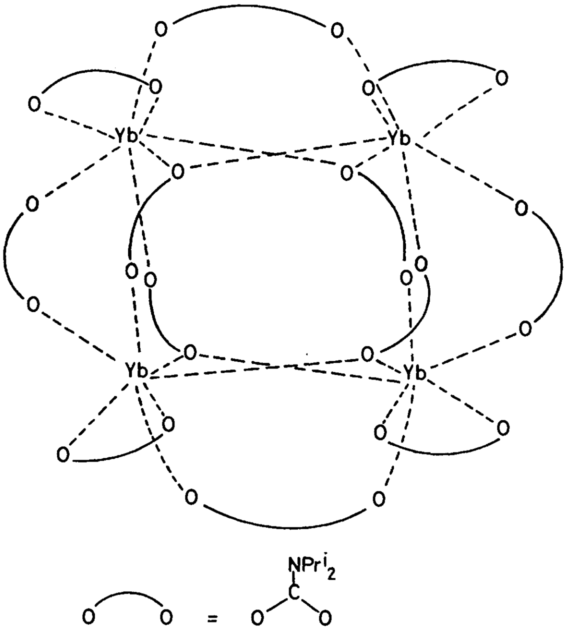


FIGURE. The tetrameric unit of $Yb_4(C_7H_{14}NO_2)_{12}$ viewed along the b axis. The methyl groups have been omitted for clarity. The broken lines represent bonds from the two nonequivalent ytterbium atoms. $' = -x, y, -1/2-z$.

The structure (see Figure) consists of discrete tetrameric units lying on a two-fold axis of the $C2/c$ space group; the ytterbium atoms are joined by bridging di-isopropylcarbamato groups of type (b) and (c), the heptaco-ordination being achieved by bonding to terminal bidentate groups of type (a).



The Yb–O distances range from 2·18(4) to 2·39(3) Å, the shortest distances being observed for type (b) ligands [2·18(4)—2·25(3) Å].



Line drawing of the tetramer $Yb_4(C_7H_{14}NO_2)_{12}$

The synthesis of the dialkylcarbamato complexes, as shown in equation (1), may be regarded as a $R_2NCO_2{}^- \rightarrow Cl^-$ exchange, the dialkylcarbamato anion being formed[1] in a rapid pre-equilibrium between CO_2 and the secondary amine. Chisholm and Extine[5] have recently recognized that what had been previously thought to be a CO_2 insertion in the M–NR_2 bond to give M–O_2CNR_2 should in fact be considered as a R_2NH promoted displacement of $NR_2{}^-$ from the co-ordination sphere of the metal.

Although the dialkylcarbamato complexes of ytterbium do not show any appreciable loss of CO_2, the carbamato groups are quickly displaced when the complexes are

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† The presence of heptane was established by elemental analysis and thermal decomposition; at this stage of the refinement its crystallographic location has not been completely solved.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

treated with proton-active substances. This reaction has been used for further characterisation of these complexes and has also been utilized for the preparation of Yb^{III} compounds otherwise difficult to obtain, such as the YbI_6^{3-} anion [see equation (2)].

$$Yb(O_2CNR_2)_3 + 6\,HI \rightarrow 3\,CO_2 + (NH_2R_2^+)_3YbI_6^{3-} \qquad (2)$$

This method of preparation of the hexaiodoytterbate anion is an alternative to that reported in the literature[6,7] and does not require the preliminary synthesis of the $YbCl_6^{3-}$ anion.

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