NN-Dialkylcarbamato-complexes of 4*f* Elements*

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By reaction of the anhydrous metal(III) halide with a secondary amine and carbon dioxide in a hydrocarbon solvent, the first *NN*-dialkylcarbamato-complexes of lanthanide metals have been prepared, $[M_n(O_2CNR_2)_{3n}]$ (M = Yb or Er). In the case of the ytterbium derivative with R = Pr^i, the crystal and molecular structure has been solved by *X*-ray diffraction methods. The complex is a tetramer, $[\{Yb(O_2CNPr^i_2)_3\}_4]\cdot 2C_7H_{16}$; crystals are monoclinic, space group *C*2/*c*, with *a* = 29.069(5), *b* = 19.591(3), *c* = 23.193(4) Å, β = 107.70(2)°, and *Z* = 4. The four seven-co-ordinate ytterbium atoms are joined by bridging *NN*-dialkylcarbamato-groups. The ytterbium derivative reacts promptly with proton-active substances yielding the appropriate complex salts, with quantitative evolution of carbon dioxide.

Binary *NN*-dialkylcarbamato-complexes are known for the early transition-metal cations, such as titanium(IV),[1] zirconium(IV), vanadium(IV), niobium(V), tantalum(V),[2] tungsten(III),[3] and uranium(IV).[4] For several transition elements *NN*-dialkylcarbamato-complexes are still unknown and the same is true for 4*f* elements, with the sole exception of tris(*NN*-diisopropylcarbamato)ytterbium(III), which was reported in an earlier preliminary communication [5] from these Laboratories. We now report the full details of the synthesis and of the crystal and molecular structure of this compound, together with further preparative work concerning *NN*-dialkylcarbamato-derivatives of lanthanides and their properties.

Experimental

All manipulations and reactions involving metal complexes were carried out under a strictly anhydrous nitrogen or carbon dioxide atmosphere. Infrared spectra were measured with a Perkin-Elmer model 283 instrument equipped with a grating monochromator. Magnetic susceptibilities were measured with a magnetic balance (Faraday method), using $CuSO_4\cdot 5H_2O$ as calibrant. Solvents were carefully dried by conventional methods prior to use. The lanthanide(III) chlorides used in this work were prepared by heating the oxide with ammonium chloride according to literature methods.[6]

Preparation of $[Yb(O_2CNEt_2)_3]$.—By operating under a nitrogen atmosphere, anhydrous ytterbium(III) chloride (3.84 g, 13.75 mmol) was suspended in heptane (200 cm^3) and treated with anhydrous diethylamine (6.4 g, 87.5 mmol) for *ca.* 1 h at room temperature. The system was then connected to a vacuum line and carbon dioxide was introduced into the flask. The mixture was stirred at room temperature for 4 d and during this time the internal total pressure of the system was kept constant to 1 atm with carbon dioxide. The reaction mixture was filtered and the colourless solid so obtained was washed several times with dichloromethane, until the test for chloride ion was negative. The residual colourless solid was dried *in vacuo* (yield 71%) and analysed without further purification (Found: C, 34.0; H, 5.8; CO_2, 24.6; N, 7.7. Calc. for $C_{15}H_{30}N_3O_6Yb$: C, 34.6; H, 5.8; CO_2, 25.3; N, 8.1%). The compound is decomposed by dilute sulphuric acid (20%) with quantitative evolution of carbon dioxide. Magnetic susceptibility at room temperature: $\chi_M^{corr} = 7\,645 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -222×10^{-6} c.g.s.u., corresponding to $\mu_{eff.} = 4.23$ B.M.).

Preparation of $[Yb(O_2CNPr^i_2)_3]$.—By operating under conditions similar to those used for the synthesis of the corresponding ethyl derivative, anhydrous ytterbium(III) chloride (3.29 g, 11.8 mmol) was treated with anhydrous di-isopropylamine (7.20 g, 71.2 mmol) in toluene (100 cm^3). After stirring for 3 h at room temperature under a nitrogen atmosphere, the resulting mixture was treated with carbon dioxide and stirred for 4 d. The reaction mixture was filtered and the resulting solid was extracted in a continuous extraction apparatus under nitrogen with pentane. From the pentane extract, 4.51 g (yield 63%) of the colourless compound separated out, which was collected by filtration and dried *in vacuo* (Found: C, 41.2; H, 6.8; N, 6.6; Yb, 28.4. Calc. for $C_{21}H_{42}N_3O_6Yb$: C, 41.7; H, 7.0; N, 6.9; Yb, 28.6%). Extraction with n-heptane under reduced pressure gave crystals of the product containing lattice heptane. These crystals were used for the molecular structure determination by *X*-ray diffraction. [Found: C, 44.5; H, 7.7; Yb, 26.8. Calc. for $C_{21}H_{42}N_3O_6Yb\cdot 0.5C_7H_{16}$: C, 44.9; H, 7.7; Yb, 26.4%). The product without lattice heptane was monomeric by cryoscopy in benzene (Found: *M* = 561. Calc. *M* = 606). Magnetic susceptibility at room temperature: $\chi_M^{corr} = 7\,576 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -309×10^{-6} c.g.s.u., corresponding to $\mu_{eff.} = 4.21$ B.M.). In C_2Cl_4 solution the compound has bands at 1 625w, 1 610w, 1 605m, 1 545m, 1 495s, 1 470m, 1 450m, 1 385m, and 1 360s cm^{-1}. In $[C_2ClF_3]_n$ mulls, bands were observed at 1 605s, 1 535s, 1 490vs, 1 460s, 1 370s, 1 350vs, 1 220m, and 1 205m cm^{-1}.

Preparation of $[Er(O_2CNPr^i_2)_3]$.—Anhydrous erbium(III) chloride (1.66 g, 6.07 mmol) in heptane (100 cm^3) was treated under a nitrogen atmosphere with di-isopropylamine (3.67 g, 36.3 mmol) for *ca.* 3 h. The mixture was then stirred under a carbon dioxide atmosphere for 2 d. After filtration, the erbium(III) carbamato-complex crystallized out from the filtrate by cooling to *ca.* 5 °C. The crude solid from the reaction was extracted with heptane under reduced pressure to obtain a second crop of the compound (total yield 4.8%) as pink crystals (Found: C, 41.5; H, 7.5. Calc. for $C_{21}H_{42}ErN_3O_6$: C,

* *Supplementary data available* (No. SUP 23460, 24 pp.): structure factors, thermal parameters, ligand geometries, i.r. data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: 1 atm = 101 325 N m^{-2}; 1 B.M. = 0.927×10^{-3} A m^2.

Table 1. Final fractional atomic co-ordinates ($\times 10^4$ for Yb and O and $\times 10^3$ for C and N) with estimated standard deviations in parentheses *

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Yb(1)	681(1)	3 009(1)	7 053(1)	C(71)	25(3)	504(4)	841(3)
Yb(2)	761(1)	1 883(1)	8 396(1)	C(22)	114(3)	102(3)	699(3)
O(11)	658(10)	3 015(13)	8 076(11)	C(32)	147(3)	36(4)	722(3)
O(21)	7(14)	3 577(16)	8 162(14)	C(42)	135(3)	133(4)	649(3)
O(12)	611(12)	1 917(18)	7 326(13)	C(52)	47(2)	37(3)	643(3)
O(22)	−24(13)	1 347(14)	6 831(13)	C(62)	10(3)	59(3)	582(3)
O(13)	1 488(12)	2 125(17)	8 375(14)	C(72)	20(3)	−14(4)	674(3)
O(23)	1 427(14)	2 736(18)	7 523(16)	C(23)	249(2)	211(3)	866(3)
O(14)	275(13)	2 541(17)	6 155(15)	C(33)	252(3)	250(4)	928(4)
O(24)	−497(13)	2 375(16)	5 901(14)	C(43)	244(3)	136(4)	866(3)
O(15)	1 224(14)	1 308(19)	9 248(16)	C(53)	240(3)	297(4)	779(3)
O(25)	926(14)	775(18)	8 319(16)	C(63)	271(4)	350(6)	808(4)
O(16)	879(17)	4 122(22)	7 244(20)	C(73)	260(4)	250(6)	749(5)
O(26)	1 038(15)	3 613(21)	6 456(18)	C(24)	35(3)	273(5)	504(4)
C(11)	44(2)	354(3)	826(2)	C(34)	59(4)	209(6)	497(5)
C(12)	42(2)	140(3)	704(3)	C(44)	30(3)	344(5)	468(4)
C(13)	169(3)	247(3)	801(3)	C(54)	−55(3)	226(5)	473(4)
C(14)	−8(2)	243(2)	580(2)	C(64)	−90(3)	280(4)	451(4)
C(15)	125(2)	73(3)	893(3)	C(74)	−57(4)	157(6)	453(5)
C(16)	111(3)	410(5)	680(4)	C(25)	170(4)	15(4)	986(4)
N(1)	76(1)	397(2)	863(2)	C(35)	211(4)	54(6)	1 001(5)
N(2)	65(2)	93(2)	679(2)	C(45)	128(3)	15(5)	1 018(4)
N(3)	216(2)	249(2)	815(2)	C(55)	135(3)	−47(5)	880(4)
N(4)	−12(2)	250(2)	517(2)	C(65)	185(4)	−64(5)	874(4)
N(5)	140(2)	14(3)	920(3)	C(75)	110(4)	−106(5)	899(4)
N(6)	138(3)	468(4)	670(3)	C(26)	140(4)	514(6)	705(5)
C(21)	127(2)	386(3)	879(2)	C(36)	199(4)	528(5)	744(4)
C(31)	148(3)	362(4)	941(3)	C(46)	123(5)	596(8)	680(6)
C(41)	155(3)	454(4)	873(3)	C(56)	160(4)	468(6)	620(5)
C(51)	56(2)	455(3)	889(3)	C(66)	189(4)	413(6)	626(5)
C(61)	24(2)	432(3)	929(3)	C(76)	112(4)	477(5)	558(4)

* The second digit in the numbering of the atoms refers to the ligand.

42.0; H, 7.1%). Magnetic susceptibility at room temperature: $\chi_M^{corr} = 35\,400 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -309×10^{-6} c.g.s.u., corresponding to $\mu_{eff.} = 9.11$ B.M. Similar results were obtained by operating under a CO_2 pressure of 50 atm at *ca.* 120 °C. In C_2Cl_4 solution the compound has bands at 1 625w, 1 610w, 1 605m, 1 545m, 1 495s, 1 470s, 1 450m, 1 385m, and 1 360s cm^{-1}. For Nujol mulls, bands were observed at 1 600s, 1 535m, 1 490vs, 1 470s, 1 460s, 1 450s, 1 380m, and 1 350s cm^{-1}.

Reactions with Acids.—$[Yb(O_2CNEt_2)_3]$ *with* HI. The *NN*-diethylcarbamatoytterbium complex (0.70 g, 1.34 mmol) was dissolved in benzene (100 cm^3) and treated at room temperature with an excess of anhydrous HI. A prompt evolution of carbon dioxide was noted and the dark violet $[NH_2Et_2]_3[YbI_6]$ precipitated out. The hexaiodoytterbate(III) complex was collected by filtration (yield 84%). The compound is extremely sensitive to moisture (Found: C, 12.0; H, 3.2; I, 64.5. Calc. for $C_{12}H_{36}I_6N_3Yb$: C, 12.5; H, 3.1; I, 65.8%). Magnetic susceptibility at room temperature: $\chi_M^{corr} = 8\,897 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -462×10^{-6} c.g.s.u., corresponding to $\mu_{eff.} = 4.57$ B.M.).

$[Yb(O_2CNPr^i_2)_3]$ *with* HI. The *NN*-di-isopropylcarbamatoytterbium complex was similarly treated with excess anhydrous HI in toluene as solvent, yielding a substantially quantitative yield of the violet di-isopropyl derivative $[NH_2Pr^i_2]_3[YbI_6]$ (Found: C, 17.2; H, 4.1; I, 61.3; N, 3.5. Calc. for $C_{18}H_{48}I_6N_3Yb$: C, 17.4; H, 3.9; I, 61.4; N, 3.4%). Magnetic susceptibility at room temperature: $\chi_M^{corr} = 9\,010 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -533×10^{-6} c.g.s.u., corresponding to $\mu_{eff.} = 4.59$ B.M.).

$[Yb(O_2CNEt_2)_3]$ *with acetic acid.* The *NN*-diethylcarbamatoytterbium complex (1.04 g, 2.0 mmol) was dissolved in toluene (50 cm^3) and treated with an excess of acetic acid. Evolution of carbon dioxide was observed and the ytterbium(III) acetate which precipitated was collected by filtration and dried *in vacuo* (yield 67%). The analysis corresponded to the expected formula (Found: C, 21.0; H, 2.7. Calc. for $C_6H_9O_6Yb$: C, 20.5; H, 2.6%).

X-Ray Data Collection and Structure Refinement of $[\{Yb(O_2CNPr^i_2)_3\}_4]\cdot 2C_7H_{16}$.—As specified above, the crystals used for the *X*-ray diffractometric study were obtained as colourless prisms by recrystallization from heptane. These crystals had to be introduced and sealed in Lindemann capillaries under an atmosphere of nitrogen saturated with heptane vapour in order to minimize loss of lattice heptane and to avoid their subsequent collapse to a microcrystalline powder. Preliminary Weissenberg photographs showed monoclinic symmetry and two possible space groups, *Cc* or *C2/c*. The latter was chosen and confirmed by the successful refinement. Intensities were collected from a crystal of approximate dimensions 0.5 × 0.4 × 0.3 mm, mounted with the *a* axis parallel to the spindle axis of an on-line Siemens AED diffractometer using Cu-K_α radiation and the ' five-point ' technique.[7] The crystal showed some decomposition during data collection presumably due to loss of lattice heptane and a slight difference in unit-cell parameters with respect to the initial values was observed at the end of the experiment. The intensity decay was monitored by a standard reflection measured every 15 reflections. Intensities were corrected accordingly by means of a simple linear interpolation. No correction for absorption

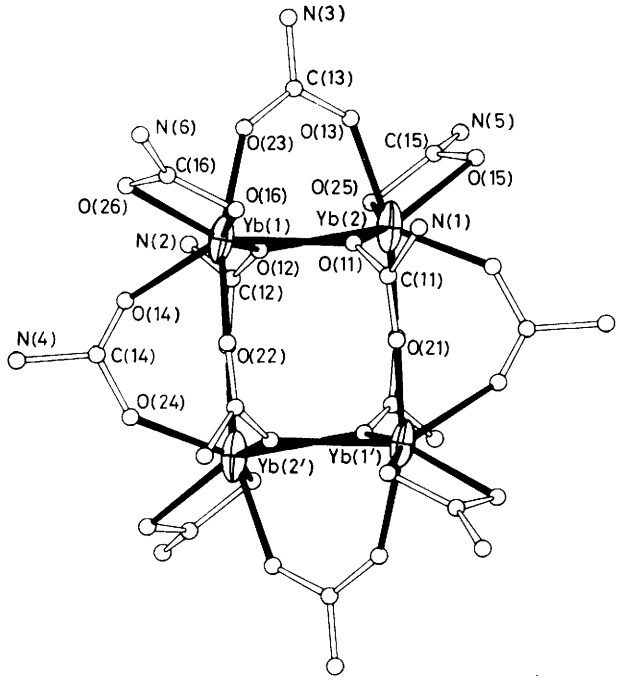


Figure 1. The tetrameric unit of $[\{Yb(O_2CNPr^i_2)_3\}_4]\cdot 2C_7H_{16}$ viewed along *b*. The isopropyl groups have been omitted for clarity

was applied due to the irregular shape of the crystal and to the intrinsic poor quality of the collected data. 7 897 Reflections were collected, 3 368 of them with $I > 4.0\sigma(I)$ [$\sigma^2(I)$ = total counts + $(0.005\ I)^2$] being used for structure solution.

The structure was solved by standard Patterson and Fourier methods. Block-matrix least-squares refinement on *F* minimizing the function $\Sigma w|F_o - F_c|^2$ was performed, which led to the final *R* factor of 0.124.[8] During the refinement, anisotropic thermal parameters were used for ytterbium only; in the calculations of the structure factors the contributions of the hydrogen atoms were neglected, whereas the correction for anomalous dispersion effects on ytterbium was performed.[9] Attempts to locate the lattice heptane by difference-Fourier maps were unsuccessful, although these maps roughly indicated the presence of one of the heptane molecules approximately in the position 0, ¼, ¼. The contributions of these molecules to the structure factors are neglected. The final positional parameters are listed in Table 1.

Crystal data. $C_{84}H_{168}N_{12}O_{24}Yb_4\cdot 2C_7H_{16}$, $M = 2\,622.9$ (including lattice heptane for tetramer), Monoclinic, space group *C*2/*c*, $a = 29.069(5)$, $b = 19.591(3)$, $c = 23.193(4)$ Å, $\beta = 107.70(2)°$, $U = 12\,583$ Å^3, $D_c = 1.384$ g cm^{-3}, $Z = 4$, Cu-K_α radiation, μ(Cu-K_α) = 59 cm^{-1}, $\lambda = 1.541\ 78$ Å, $F(000) = 5\,376$, θ—2θ scan technique, 2θ range = 6—110°, 317 independent variables, unit weights.

Results and Discussion

Anhydrous chlorides of erbium(III) and ytterbium(III) undergo a metathetical reaction with the *NN*-dialkylcarbamato-anion to give the corresponding *NN*-dialkylcarbamato-complexes, see equations (1) and (2) (M = Er^{III} or Yb^{III}, R = alkyl).

$$CO_2 + 2NHR_2 \rightleftharpoons [NH_2R_2][O_2CNR_2] \quad (1)$$

$$3[NH_2R_2][O_2CNR_2] + MCl_3 \longrightarrow 3[NH_2R_2]Cl + [M(O_2CNR_2)_3] \quad (2)$$

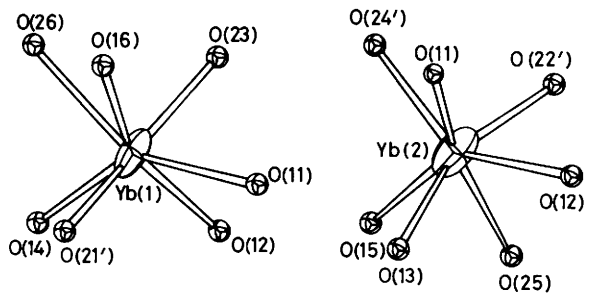
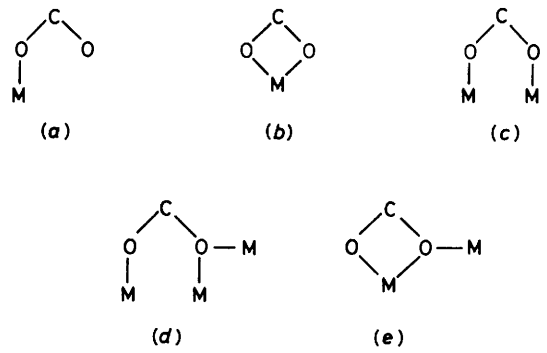


Figure 2. View of the seven-co-ordinate ytterbium atoms

The reaction occurs in hydrogen solvents, either aliphatic or aromatic, and due to the extremely low solubility of the dialkylammonium chloride in the reaction medium, the isopropyl lanthanide complex can be separated by filtration of the reaction mixture and its yields increased by extraction with a low-boiling-point aliphatic hydrocarbon. On the other hand, in the case of the less soluble ethyl derivative, $[Yb(O_2CNEt_2)_3]$, the latter was recovered by filtration and purified by dissolving the admixed $[NH_2Et_2]Cl$ in dichloromethane.

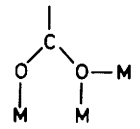
The molecular structure of the isopropyl ytterbium derivative is shown in Figure 1. It consists of discrete tetrameric units possessing a two-fold axis of symmetry. The ytterbium atoms are joined by bridging carbamato-groups, (*c*) and (*d*), Terminal and chelating groups, (*b*), are also present, while unidentate groups (*a*), which are more frequently encountered in dialkylcarbamato-complexes of *d* transition elements (see below), are absent in this compound. The bonding arrangement (*e*) has been found in $[U_4O_2(O_2CNEt_2)_{12}]$.[10]



Some of these bonding arrangements have been found for carboxylato-[11] and carbonato-complexes[12] of transition elements, which is expected in view of the fact that *NN*-dialkylcarbamato-, carboxylato-, and carbonato-complexes belong to the same category of compounds containing the ligating group $O_2C{-}X$ (X = NR_2, R, and O respectively). The two non-equivalent ytterbium atoms are seven-co-ordinate, as shown in Figure 2, and the geometry is best described as that of a capped trigonal prism, both for Yb(1) and Yb(2). Other oxygen-co-ordinated complexes have been found to contain seven-co-ordinate ytterbium(III) such as $[Yb(acac)_3]\cdot H_2O$ (acac = acetylacetonate),[13] $[Yb(acac)_3]\cdot H_2O\cdot 0.5C_6H_6$,[14] and $[Yb(acac)_3]\cdot L$ (L = 4-aminopent-3-en-2-one).[15] The evidently strong tendency of oxygen-co-ordinated ytterbium(III) to achieve seven-co-ordination[16] may well explain the observed existence of the unique type of bridging *NN*-dialkylcarbamato group (*d*). The unidentate type of *NN*-dialkylcarbamato group, type (*a*), so frequently encountered with *d* transition elements, *e.g.* in $[Nb(O_2CNMe_2)_5]$,[2,17] $[W_2(O_2CNMe_2)_6]$,[2,3] and $[W(NMe_2)_3(O_2CNMe_2)_3]$,[18] was

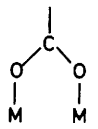
Table 2. Interatomic distances (Å) and angles (°) for $[\{Yb(O_2CNPr^i_2)_3\}_4]\cdot 2C_7H_{16}$

(*i*) Ytterbium geometry



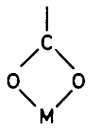
(*d*)

Yb(1)–O(11)	2.39(1)	Yb(2)–O(11)	2.33(1)
Yb(1)–O(21′)	2.21(2)	Yb(2)–O(12)	2.39(2)
Yb(1)–O(12)	2.26(2)	Yb(2)–O(22′)	2.30(2)



(*c*)

Yb(1)–O(23)	2.18(2)	Yb(2)–O(13)	2.18(2)
Yb(1)–O(14)	2.25(2)	Yb(2)–O(24′)	2.22(2)



(*b*)

Yb(1)–O(16)	2.26(2)	Yb(2)–O(15)	2.32(2)
Yb(1)–O(26)	2.30(3)	Yb(2)–O(25)	2.24(2)

(*ii*) Bond angles around the oxygen atoms *

Yb(1)–O(11)–C(11)	119(1)	Yb(2)–O(11)–C(11)	131(1)
Yb(1′)–O(21)–C(11)	146(1)	Yb(2)–O(12)–C(12)	116(2)
Yb(1)–O(12)–C(12)	133(2)	Yb(2′)–O(22)–C(12)	147(2)
Yb(1)–O(23)–C(13)	142(2)	Yb(2)–O(13)–C(13)	137(2)
Yb(1)–O(14)–C(14)	149(2)	Yb(2′)–O(24)–C(14)	136(1)
Yb(1)–O(16)–C(16)	88(3)	Yb(2)–O(15)–C(15)	93(1)
Yb(1)–O(26)–C(16)	91(4)	Yb(2)–O(25)–C(15)	94(1)
Yb(1)–O(11)–Yb(2)	105.7(5)	Yb(2)–O(12)–Yb(1)	108.3(6)

* Primed atoms signify the transformation, x, y, $3/2 + z$. The second digit in the numbering of the atoms refers to the ligand.

found neither in this ytterbium(III) derivative nor in the uranium(IV) complex $[U_4O_2(O_2CNEt_2)_{12}]$.[10] Both the larger value of the ionic radius for 4*f* and 5*f* ions and their tendency to expand the co-ordination sphere are presumably responsible for this.

As shown in Table 2, the ytterbium–oxygen distances range from 2.18(2) to 2.39(2) Å. In the acac complexes of ytterbium(III), the Yb–O distances range between 2.147(17) and 2.358(13) Å for $[Yb(acac)_3]\cdot H_2O$,[13] between 2.204(12) and 2.347(11) Å for $[Yb(acac)_3]\cdot H_2O\cdot 0.5C_6H_6$,[14] and between 2.18(2) and 2.29(2) Å for $[Yb(acac)_3]\cdot L$.[15] On examination of the data of Table 2 it may be seen that, in spite of the low accuracy of the structure determination, there are significant trends in the Yb–O distances. Specifically, the longer distances belong to the three-co-ordinate oxygen atom of the carbamato-ligand of type (*d*), which is expected in view of the lower availability of electron density on oxygen for bonding. On the other hand, the shortest distances and presumably the strongest bonds are those within the bridging carbamato-ligand of type (*c*). For the two types of ligands which the present ytterbium compound has in common with $[U_4O_2(O_2CNEt_2)_{12}]$, namely (*b*) and (*c*), the 4*f* and 5*f* systems behave similarly as far as internal M–O distances are concerned.

The geometry of the ligands especially for the isopropyl groups is affected by both the poor quality of the structure determination and also probably by an intrinsic crystal disorder of the carbon chains. A list of interatomic distances and bond angles within the carbamato-ligands has been deposited (SUP 23460).

The presence of lattice heptane in our compound was established analytically and by direct determination of the heptane obtained by thermal treatment of the crystals *in vacuo*. As already mentioned in the Experimental section, the detailed location of the heptane was not possible.

Beside establishing the existence of the *NN*-dialkylcarbamato-ligand for 4*f* transition metals, the present ytterbium complex is a valuable intermediate for the preparation of other ytterbium(III) co-ordination compounds. This is due to the elevated reactivity of the *NN*-dialkylcarbamato-group towards electrophilic reagents, especially the proton. The reaction with protons in aqueous solution was found to decompose the compound giving off carbon dioxide quantitatively, see equation (3). In non-aqueous solvents, acetic acid and hydrogen iodide were found to react according to equations (4) and (5), respectively.

$$[Yb(O_2CNR_2)_3] + 3H^+ \longrightarrow Yb^{3+} + 3CO_2 + 3NHR_2 \quad (3)$$

$$[Yb(O_2CNR_2)_3] + 3MeCO(OH) \longrightarrow [Yb(O_2CMe)_3] + 3CO_2 + 3NHR_2 \quad (4)$$

$$[Yb(O_2CNR_2)_3] + 6HI \longrightarrow [NH_2R_2]_3[YbI_6] \quad (5)$$

Reaction (3) was used for analytical purposes. Reaction (4) can be regarded as an alternative method for the preparation of anhydrous ytterbium(III) acetate,[19] while reaction (5) is particularly useful since it gives a substantially quantitative yield of the unstable [20] hexaiodoytterbate(III) anion. The preparation of the $[YbI_6]^{3-}$ anion was carried out in hydrocarbon solvents, *i.e.* under conditions of no competition by

the solvent for the co-ordination sphere of the lanthanide. Moreover, this preparation of the complex anion does not require the previous isolation [20] of the hexachloroytterbate anion.

Several anhydrous lanthanide chlorides have been treated with carbon dioxide and secondary amines in hydrocarbon solvents in attempts to prepare the corresponding *NN*-dialkylcarbamato-complexes. Attempts were also made under carbon dioxide pressure and at temperatures around 100 °C. Only erbium(III) chloride could be converted to the corresponding di-isopropylcarbamato-complex in small yields. We believe that the observed failure of several lanthanide chlorides to react is probably due to some kinetic effects rather than to a specific thermodynamic instability of some of the *NN*-dialkylcarbamato-complexes. Erbium and ytterbium are in the second part of the lanthanide series and their ionic radii (0.96 and 0.94 Å, respectively [21]) are very close to that of uranium(IV) (0.97 Å) and larger than those of early *d* transition metal cations, for which *NN*-dialkylcarbamato-complexes are known.[1-3] This fact and the great flexibility of bonding for the O_2CNR_2 grouping should assure the possibility of synthesizing other complexes of the lanthanide elements, once their existence has been established by the present work.

Tris(di-isopropylcarbamato)ytterbium(III) has an apparent molecular weight in benzene corresponding to that of the monomeric species. We believe that this is due to the non-ideality of these solutions. In fact, the conversion from a tetrameric to a monomeric structure would require a considerable degree of bonding rearrangement, which seems to be unlikely in a poorly basic solvent such as benzene. It is in fact remarkable that the i.r. spectrum of $[\{Yb(O_2CNPr^i_2)_3\}_4]$ in tetrachloroethylene solution is substantially identical in the 1 200—1 800 cm^{-1} region to that in Nujol, thus suggesting that no significant structural rearrangement involving the *NN*-dialkylcarbamato-groups is occurring from solid state to solution.

No crystals appropriate for *X*-ray analysis could be prepared of the erbium(III) carbamato-complex. Our structural information must therefore come solely from i.r. data. A compendium of the available solid-state structural data and solution i.r. data in the 1 800—1 200 cm^{-1} region for known carbamato-complexes of transition elements has been deposited (see SUP 23460). Here it will suffice to note that the i.r. spectrum of the erbium(III) derivative is substantially identical with that of the ytterbium(III) analogue, both as mulls and in tetrachloroethylene solution, thus suggesting that the two complexes should have very similar structures.

The magnetic susceptibility data for the compounds reported in this paper are in agreement with the available data reported in the literature for both ytterbium(III) [22,23] (a f^{13} system) and erbium(III) [23] (a f^{11} system).

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References

1 G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc. A*, 1970, 2550.
2 M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 782.
3 M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, 1977, **16**, 603.
4 F. Calderazzo, G. Dell'Amico, R. Netti, and M. Pasquali, *Inorg. Chem.*, 1978, **17**, 471 and refs. therein.
5 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1979, 1103.
6 J. B. Reed, B. S. Hopkins, and L. F. Audrieth, *Inorg. Synth.*, 1939, **1**, 28.
7 W. Hoppe, *Acta Crystallogr., Sect. A*, 1969, **25**, 67.
8 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
9 D. T. Cromer, *Acta Crystallogr.*, 1965, **18**, 17.
10 F. Calderazzo, G. Dell'Amico, M. Pasquali, and G. Perego, *Inorg. Chem.*, 1978, **17**, 474.
11 C. Oldham, *Prog. Inorg. Chem.*, 1968, **10**, 223; G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
12 P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1913; G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 586; H. C. Freeman and G. Robinson, *ibid.*, 1965, 3194.
13 J. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, *Inorg. Chem.*, 1969, **8**, 22.
14 E. D. Watkins, J. A. Cunningham, T. Phillips, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, 1969, **8**, 29.
15 M. F. Richardson, P. W. R. Corfield, D. E. Sands, and R. E. Sievers, *Inorg. Chem.*, 1970, **9**, 1632.
16 D. L. Keppert, *Prog. Inorg. Chem.*, 1979, **25**, 41.
17 M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, 1975, **97**, 1623.
18 M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, 1974, **96**, 6214.
19 J. A. Seaton, F. G. Sherif, and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, 1959, **9**, 222; J. R. Witt and E. I. Onstott, *ibid.*, 1962, **24**, 637; G. Adachi and E. A. Secco, *Can. J. Chem.*, 1972, **50**, 3100.
20 J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2053; J. L. Ryan, *Inorg. Synth.*, 1974, **15**, 225.
21 L. Pauling, 'The Nature of The Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 518.
22 D. G. Karraker, *J. Chem. Phys.*, 1971, **55**, 1084.
23 P. W. Selwood, 'Magnetochemistry,' 2nd edn., Interscience, New York, 1956, pp. 140—149.

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