Inorganica Chimica Acta, *95* (1984) 247–250

N-Substituted Ethylcarbamate Complexes of Thorium(IV) and Lanthanum(III) Nitrates

G. CASOTTO, B. ZARLI, G. FARAGLIA and L. SINDELLARI

Istituto di Chimica Generale ed Inorganica dell'Università, Via Loredan 4, 35100 Padua, Italy

Received February 13, 1984

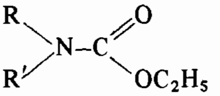
N-substituted ethylcarbamates form with thorium nitrate the complexes $Th(NO_3)_4 \cdot 3RHNC(O)OC_2H_5$ *(where* $R = CH_3$, C_2H_5, $C_6H_5(CH_3)CH$*) and with lanthanum nitrate the complexes* $La(NO_3)_3 \cdot 2RR'NC(O)OC_2H_5 \cdot 3H_2O$ *(where* $R = CH_3$, C_2H_5, $C_6H_5(CH_3)CH$; $R' = H$ *and* $R = CH_3$, C_6H_5; $R' = C_2H_5$ *or* $R = R' = CH_3$*). In addition the anhydrous* $La(NO_3)_3 \cdot 3(C_2H_5)_2NC(O)OC_2H_5$ *has been isolated. From the IR spectra it is deduced that the carbamates coordinate the metal through the carbonyl oxygen atom and that the nitrato groups act as chelated ligands.* ^1H *nmr spectral data of the complexes are reported and discussed.*

Introduction

Complexes of thorium(IV) with ligands containing the carbonyl group are widely reported in the literature; in particular adducts of thorium tetrahalides with N-substituted ureas [1] and of thorium tetrachloride [2, 3] and tetranitrate [3–5] with N-substituted amides have been studied. The stoichiometry of the complexes generally depends on the number and the bulkiness of the substituents at the nitrogen atom.

Previously we prepared and studied complexes of thorium tetrachloride with a number of ethylcarbamates, $RR'NC(O)OC_2H_5(L)$, structurally similar to the amides [6, 7]. It has been found that the ligands coordinate the metal through the carbonyl oxygen atom giving adducts of formula $ThCl_4 \cdot 3L$. Whereas the free carbamates present at room temperature free rotation around the $C\overset{\cdots}{-}N$ bond, on complexation the double bond character of the $C\overset{\cdots}{-}N$ bond increases, the ligand molecules assuming a planar configuration. When the rotation is hindered, for ligands with different substituents, such as R and R′, two geometrical isomers are possible. The ^1H nmr spectrum of $ThCl_4 \cdot 3MeEtNC(O)OEt$ in benzene shows the signals of both isomers [6], whereas $ThCl_4 \cdot 3MeHNC(O)OEt$ seems to contain the ligand in only one of the isomeric forms [7].

On this basis it appeared of interest to extend the study to complexes of thorium tetranitrate with this class of ligand. The ethylcarbamates (urethanes) used and the respective abbreviations are as follows:



$R = CH_3$; $R' = H$	(MU)
$R = R' = CH_3$	(DMU)
$R = C_2H_5$; $R' = H$	(EU)
$R = R' = C_2H_5$	(DEU)
$R = CH_3$; $R' = C_2H_5$	(MEU)
$R = C_6H_5$; $R' = C_2H_5$	(PhEU)
$R = C_6H_5(CH_3)CH$; $R' = H$	(1-pheU)
$R = C_6H_5$; $R' = H$	(PhU)
$R = R' = C_6H_5$	(DPhU)

Further, since the analogous uranium(IV) and uranyl(VI) complexes [6–8] were already known, we undertook the preparation of adducts of lanthanides in order to compare the behaviour of metals belonging to the two f-blocks towards the above donors. As part of a more complete work, the paper reports the complexes of lanthanum(III) nitrate.

Experimental

Hydrated thorium tetranitrate and lanthanum trinitrate hexahydrate were R.G. commercial products used as supplied. The ethylcarbamates were as already described [6–8]. The solvents were distilled under nitrogen: n-hexane from Na/K alloy, benzene from Na. The lanthanum complexes were purified and handled in a dry nitrogen atmosphere and stored in dry-boxes.

Preparation of the $Th(NO_3)_4$ *Complexes*

Hydrated thorium nitrate (≃2 mmol) was dissolved by stirring in the appropriate liquid ligand (20 mmol). Water was removed at reduced pressure, yielding oils which were dissolved in benzene and precipitated with n-hexane; the purification was repeated three times. With the solid 1-pheU an alternative procedure was used: a solution of hydrat-

0020-1693/84/$3.00

TABLE I. Analytical Data of the Complexes (the calculated values are in parentheses).

Compound	M.p. °C	C%	H%	N%
$\mathrm{Th(NO_3)_4 \cdot 3MU}$	–	18.4	3.5	12.3
		(18.2)	(3.4)	(12.4)
$\mathrm{Th(NO_3)_4 \cdot 3EU}$	–	21.5	4.0	11.6
		(21.6)	(4.0)	(11.8)
$\mathrm{Th(NO_3)_4 \cdot 3(1\text{-}phe\ U)}$	–	37.9	4.4	9.0
		(37.4)	(4.2)	(9.3)
$\mathrm{La(NO_3)_3 \cdot 2MU \cdot 3H_2O}$	70	16.5	3.9	11.8
		(16.4)	(4.1)	(12.0)
$\mathrm{La(NO_3)_3 \cdot 2DMU \cdot 3H_2O}$	60	19.3	4.4	11.5
		(19.6)	(4.5)	(11.4)
$\mathrm{La(NO_3)_3 \cdot 2EU \cdot 3H_2O}$	60	19.7	4.4	11.6
		(19.6)	(4.5)	(11.4)
$\mathrm{La(NO_3)_3 \cdot 2MEU \cdot 3H_2O}$	50	22.0	4.8	10.9
		(22.4)	(5.0)	(10.9)
$\mathrm{La(NO_3)_3 \cdot 3DEU}$	68	33.0	5.9	11.0
		(33.2)	(5.9)	(11.0)
$\mathrm{La(NO_3)_3 \cdot 2(1\text{-}pheU) \cdot 3H_2O}$	–	34.5	4.8	9.0
		(34.6)	(4.7)	(9.1)
$\mathrm{La(NO_3)_3 \cdot 2PhEU \cdot 3H_2O}$	65	34.9	4.5	9.2
		(34.6)	(4.7)	(9.1)

TABLE II. Some Stretching Frequencies ($\mathrm{cm^{-1}}$) of the Complexes.

Compound	ν(C=O)	ν(N–H)
$\mathrm{Th(NO_3)_4 \cdot 3MU}$	1650	3405
$\mathrm{Th(NO_3)_4 \cdot 3EU}$	1640	3390
$\mathrm{Th(NO_3)_4 \cdot 3(1\text{-}pheU)}$	1630	3375
$\mathrm{La(NO_3)_3 \cdot 2MU \cdot 3H_2O}$	1660	–
$\mathrm{La(NO_3)_3 \cdot 2DMU \cdot 3H_2O}$	1650	–
$\mathrm{La(NO_3)_3 \cdot 2EU \cdot 3H_2O}$	1655	–
$\mathrm{La(NO_3)_3 \cdot 2MEU \cdot 3H_2O}$	1645	–
$\mathrm{La(NO_3)_3 \cdot 3DEU}$	1630	–
$\mathrm{La(NO_3)_3 \cdot 2(1\text{-}pheU) \cdot 3H_2O}$	1660	–
$\mathrm{La(NO_3)_3 \cdot 2PhEU \cdot 3H_2O}$	1628	–

ed thorium nitrate ($\simeq$2 mmol) and ligand (10 mmol) in iso-propanol (40 ml) was evaporated to dryness at reduced pressure and the residue purified from benzene/n-hexane, by repeatedly washing with n-hexane.

The compounds were colourless, viscous oils which could not be induced to crystallise. They are soluble in benzene, nitromethane, acetone and alcohols and insoluble in ether, hydrocarbons and chlorinated hydrocarbons.

Preparation of the $La(NO_3)_3$ Complexes

The lanthanum nitrate complexes with liquid ligands were prepared as described above for the thorium complexes, the purification from benzene/n-hexane being carried out only one or two times to avoid decomposition. The colourless, oily proocts obtained were carefully washed with n-hexane and, after digestion and/or grinding under benzene, white crystalline solids formed in 1–2 days. The oily DEU complex immediately turned solid on washing with n-hexane. The adducts with 1-pheU or PhEU were prepared in iso-propanol as described for the thorium complex, using a molar ratio lanthanum nitrate to ligand = 1:3 instead of 1:5. The former compound was a colourless oil at room temperature which solidified on cooling and the latter a cream solid.

The complexes are soluble in nitromethane, acetone and alcohols and insoluble in benzene (except the DEU complex), ether, hydrocarbons and chlorinated hydrocarbons.

The complexes are listed in Table I along with the analytical data.

The IR spectra in the region 4000–400 $\mathrm{cm^{-1}}$ were recorded on a Perkin-Elmer mod. 683 spectrophotometer using Nujol mulls of the solids or films of the pure liquids between KBr plates. The significant bands are reported in Tables II and III.

The ^{1}H nmr spectra were taken on a Varian FT 80 A spectrometer.

Results and Discussion

Among the ethylcarbamates used, only MU, EU and 1-pheU(L) form adducts of formula $\mathrm{Th(NO_3)_4 \cdot 3L}$ with thorium nitrate. The stoichiometry corres-

TABLE III. Fundamental, Combination and Overtone Frequencies (cm^{-1}) of the Nitrato Group.

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$2\nu_2$	$\nu_2 + \nu_1$	$\nu_2 + \nu_4$	$\nu_2 + \nu_3$	$\nu_2 + \nu_5$
$Th(NO_3)_4 \cdot 3MU$	1520[a]	1030[a]	745	1290[a]	705	810	2050	2540	2290	1770	1740
$Th(NO_3)_4 \cdot 3EU$	1510[a,b]	1028[a]	743	1285	703	810	2040	2540	2290	1765	1740
$Th(NO_3)_4 \cdot 3$(1-pheU)	1520[a]	1022	742	1285	N.O.[c]	809	2043	2540	2290	1765	1737[b]
$La(NO_3)_3 \cdot 2MU \cdot 3H_2O$	1500	1030[a] 1040	735	1295[a]	722	818	2060	2510	2300 2330 2350	1762	N.O.[c]
$La(NO_3)_3 \cdot 2DMU \cdot 3H_2O$	1500	1032 1038	733	1300	720	818	2060	2508	2320	1770	1730
$La(NO_3)_3 \cdot 2EU \cdot 3H_2O$	1490	1030[a] 1040	737	1290[a]	712 723	818	2055 2080	2510	2290 2320 2360 2380	1760[b]	1735[b]
$La(NO_3)_3 \cdot 2MEU \cdot 3H_2O$	1510	1032 1040	735	1300[a]	710 722	818	2060	2510	2300	1760	1738
$La(NO_3)_3 \cdot 3DEU$	1492[a]	1015[a] 1025	752	1280[a]	N.O.[c]	815 830 840	2040 2060	2500	2293	1760	1730
$La(NO_3)_3 \cdot 2$(1-pheU)$\cdot 3H_2O$	1500	1030	735	1300[a]	713	818	2050	2515	2300	1758	1738
$La(NO_3)_3 \cdot 2PhEU \cdot 3H_2O$	1510[a,b]	N.O.[c]	738	N.O.[c]	725	818	2045	2515	2290	1760	N.O.[c]

[a] The ligand contributes to this absorption. [b] Tentative assignment. [c] Band not observed.

ponds to that of the complexes with N-monosubstituted amides [4, 5] and with diphenylsulphoxide [9]. The isolated compounds are stable non-hygroscopic oils. Thorium nitrate does not react under various experimental conditions with PhEU, PhU and DPhU, whereas with the N-dialkylcarbamates oils were isolated, whose elemental analysis data did not allow the assignment of any reasonable stoichiometry.

The lanthanum nitrate complexes are solids of general formula $La(NO_3)_3 \cdot 2L \cdot 3H_2O$, where L = MU, DMU, EU, MEU or PhEU. The corresponding 1-pheU complex is liquid at room temperature. DEU forms the adduct $La(NO_3)_3 \cdot 3DEU$ which shows no water absorption in the 3600–3200 cm^{-1} region. Complexes with such a stoichiometry have already been prepared with phosphine oxides [10, 11] and arsine oxides [12]. Every attempt to obtain complexes with DPhU and PhU was unsuccessful because the former does not react with lanthanum nitrate and the latter gives a compound of uncertain stoichiometry. The complexes, with the exception of the PhEU and the 1-pheU ones, are hygroscopic and decompose in air progressively releasing ligand molecules, the final product being lanthanum nitrate with an undefined number (5–6) of water molecules.

The IR spectra of all the compounds indicate that the ethylcarbamates bind the metal through the carbonyl oxygen: the C=O bond stretching frequencies of the complexes (Table II) are considerably lower (40–70 cm^{-1}) than the corresponding ones (around 1700 cm^{-1}) of the free ligands. The IR spectra show the presence of bidentate chelated nitrato groups in accordance with the literature [13, 14] (Table III). The N–H bond stretching frequencies, about 3330 cm^{-1} for the free ligands, rise towards 3400 cm^{-1} in the thorium complexes (Table II). The high values of this frequency, comparable with the corresponding one of $UO_2(NO_3)_2 \cdot 2$ethylcarbamate, suggest the virtual absence of hydrogen bonds as found for the uranyl derivative by a structure determination [15].

The IR spectra of the lanthanum hydrated complexes do not allow one to ascertain whether the water molecules are coordination or lattice water, because the weak bands diagnostic of coordination water fall in the 1000–500 cm^{-1} region [16, 17] where strong ligand absorptions are present. However, in our opinion, water probably binds the metal: the crystal structure of $La(NO_3)_3 \cdot 6H_2O$, the starting material in our preparations, demonstrates that the central atom is eleven coordinated by three chelated nitrato groups and five water molecules, the sixth one being lattice water [18]. It is reasonable to suppose that on complexation two ethylcarbamate molecules replace two water molecules in the first coordination sphere without change in the coordination number of the metal. The water to carbamate ratio in the complexes was determined by ^1H nmr spectra in deuterated acetone. In this solvent the complexes release the ligand, in fact each spectrum coincides with that of the corresponding free ethylcarbamate. Acetone may replace the ligand, but not water [19] whose protons give a signal in the 3–4.5 ppm region.

The 1:3 complexes of either thorium or lanthanum are stable in benzene solution, the ^1H nmr spectra consisting of generally sharp signals indicative of coordinated ligand. For $La(NO_3)_3 \cdot 3DEU$ the assignments are (ppm): $O{-}\mathit{CH}_2{-}CH_3$, 4.22; $O{-}CH_2{-}\mathit{CH}_3$, 1.01; $N{-}\mathit{CH}_2{-}CH_3$, 2.71–3.22; $N{-}CH_2{-}\mathit{CH}_3$, 0.75. The two well separated signals due to the NEt_2 methylene protons clearly demonstrate restricted rotation around the $C\overset{\cdot\cdot\cdot}{-}N$ bond of the ligand; whereas for free DEU these protons give a single broad signal at 3.05 ppm, the coordination through the carbonyl oxygen leads to magnetical non-equivalence of the NEt_2 groups with a behaviour similar to that of $UO_2(NO_3)_2 \cdot 2DEU$ [8]. The spectra of $Th(NO_3)_4 \cdot 3L$ (L = MU, EU) show, like that of $ThCl_4 \cdot 3MU$ [7], one signal for each proton group. The values are (ppm): $Th(NO_3)_4 \cdot 3MU$ = $O{-}\mathit{CH}_2{-}CH_3$, 4.09; $O{-}CH_2{-}\mathit{CH}_3$, 0.87; $N{-}CH_3$, 1.95. $Th(NO_3)_4 \cdot 3EU$ = $O{-}\mathit{CH}_2{-}CH_3$, 4.12; $O{-}CH_2{-}\mathit{CH}_3$, 0.91; $N{-}\mathit{CH}_2{-}CH_3$, 2.62; $N{-}CH_2{-}\mathit{CH}_3$, 0.71. $Th(NO_3)_4 \cdot 3(1\text{-pheU})$ = $O{-}\mathit{CH}_2{-}CH_3$, 4.03; $O{-}CH_2{-}\mathit{CH}_3$, 0.81; $N{-}CHPh{-}\mathit{CH}_3$, 1.18; $N{-}\mathit{CH}Ph{-}CH_3$, 4.37. It is seen that coordination causes an upfield shift ($\simeq$0.5 ppm) of the $N{-}CH_3$, $N{-}\mathit{CH}_2{-}CH_3$ and $N{-}\mathit{CH}Ph{-}CH_3$ resonances with respect to the free ligand.

In conclusion, whereas only the N-alkyl monosubstituted carbamates form complexes with thorium, in the series of the lanthanum complexes DEU appears to be the strongest ligand; it replaces all the water molecules present in the starting material demonstrating a higher coordinating ability than the other carbamates, probably due to a large inductive effect of the two N-ethyl groups which enhances the electron donation from the carbonyl oxygen.

Acknowledgements

The Authors thank the Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R. of Padua for financial aid and Mr. L. Turiaco, Mr. F. Braga, Mrs. T. Visentin and Mrs. B. Vittadello for technical assistance.

References

1 K. W. Bagnall, J. G. H. du Preez and M. L. Gibson, *J. Chem. Soc. (A),* 2124 (1971), and references therein.
2 K. W. Bagnall, D. Brown and P. J. Jones, *J. Chem. Soc. (A),* 741 (1966), and references therein.
3 K. W. Bagnall, D. Brown, P. J. Jones and P. S. Robinson, *J. Chem. Soc.,* 2531 (1964), and references therein.
4 K. W. Bagnall and O. V. Lopez, *J. Chem. Soc., Dalton Trans.,* 1409 (1975), and references therein.
5 K. W. Bagnall, O. V. Lopez and D. Brown, *J. Inorg. Nucl. Chem., 38,* 1997 (1976), and references therein.
6 B. Zarli, G. Faraglia, L. Sindellari and G. Casotto, *Transition Met. Chem., 6,* 17 (1981).
7 G. Faraglia, B. Zarli, L. Sindellari and G. Dall'Olio, *Inorg. Chim. Acta, 19,* 39 (1976).
8 B. Zarli, G. Casotto, L. Sindellari and G. Faraglia, *Inorg. Chim. Acta, 31,* 5 (1978).
9 B. C. Smith and M. A. Wassef, *J. Chem. Soc. (A),* 1817 (1968).
10 D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem., 29,* 1745 (1967).
11 V. K. Manchanda, K. Chander, N. P. Singh and G. M. Nair, *J. Inorg. Nucl. Chem., 39,* 1039 (1977).
12 D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem., 29,* 2965 (1967).
13 J. I. Bullock, *J. Inorg. Nucl. Chem., 29,* 2257 (1967).
14 G.Topping, *Spectrochim. Acta, 21,* 1743 (1965).
15 R. Graziani, G. Bombieri, E. Forsellini, S. Degetto and G. Marangoni, *J. Chem. Soc., Dalton Trans.,* 451 (1973).
16 W. Radecka-Paryzek, *Inorg. Chim. Acta, 45,* L147 (1980).
17 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, London, 1963, p. 156.
18 B. Eriksson, L. O. Larsson, L. Niinistö and J. Valkonen, *Inorg. Chem., 19,* 1207 (1980).
19 E. E. Zaev and L. M. Khalilov, *Zhur. Strukt. Khim., 21,* 53 (1980).