Carbamoyl methyl sulfoxide compounds of lanthanum (III) nitrate. Crystal and molecular structure of $[La(NO_3)_3\{C_6H_5SOCH_2CON(C_4H_9)_2\}_2]$.

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Carbamoyl methyl sulfoxide compounds of lanthanum (III) nitrate of the type $[La(NO_3)_3L_2]$ (where L = $C_6H_5SOCH_2CON(^iC_3H_7)_2$, $C_6H_5SOCH_2CON(C_4H_9)_2$ $C_6H_5SOCH_2CON(^iC_4H_9)_2$) have been synthesised and characterised. The structure of the compound $[La(NO_3)_3(C_6H_5SOCH_2CON(C_4H_9)_2)_2]$ shows that the $C_6H_5SOCH_2CON(C_4H_9)_2$ bonds through both the sulfoxo and carbamoyl oxygen atoms to the lanthanum(III) nitrate and acts as a bidentate chelating ligand.

Keywords: bi-functional ligand, carbamoyl methyl sulfoxide, lanthanum(III) nitrate, X-ray structure

The coordination[1] properties of neutral bi-functional and tri-functional ligands with the lanthanide and actinide ions are very important to understand the nature of species extracted during the solvent extraction[2] separation of these ions from the highly acidic nuclear waste solution. We reported recently the extraction and coordination studies of some new bi-functional ligands containing the sulfoxo and carbamoyl groups (carbamoyl methyl sulfoxide, CMSO) with lanthanide and actinide ions.[3] The extraction and coordination properties of these ligands are different from those of the mono-functional sulfoxides and amides.[4] In continuation of our research on the synthesis and coordination chemistry of new bi-functional ligands with lanthanide and actinide ions,[3,5] we report here our studies on the compounds of carbamoyl methyl sulfoxide with lanthanum (III) nitrate.

Results and discussion

The reaction of $[La(NO_3)_3.6H_2O]$ with an excess of $C_6H_5SOCH_2CONR_2$ (R = $^iC_3H_7$, C_4H_9 or $^iC_4H_9$) in ethyl acetate yielded the compounds $[La(NO_3)_3(C_6H_5SOCH_2CONR_2)_2]$. The carbon, hydrogen and nitrogen analysis revealed that the ligand to metal ratio is 2 : 1 in all these compounds. The IR spectra of these compounds show that the water molecules from the starting compound $[La(NO_3)_3.6H_2O]$ have been completely replaced by the $C_6H_5SOCH_2CONR_2$ ligands. The spectra further show that the $C_6H_5SOCH_2CONR_2$ ligands bond through both the sulfoxo and carbamoyl oxygen atoms to the lanthanum (III) nitrate. The observed frequency differences for the sulfoxo ($\Delta\nu_{SO}$ = 56 cm^{-1}) and carbamoyl ($\Delta\nu_{CO}$ = 42 cm^{-1}) groups (where $\Delta\nu_{SO}$ or $\Delta\nu_{CO}$ = $\nu_{\text{free ligand}}$ - $\Delta\nu_{\text{complex}}$) agree well with the supposition that the sulfoxo[4,5a] or carbamoyl groups[4,5a,5b] bond directly to the lanthanum(III) nitrate in the reported compounds. The peaks at 1523, 1307, 1275 cm^{-1} show the presence of nitrate groups in all these compounds.

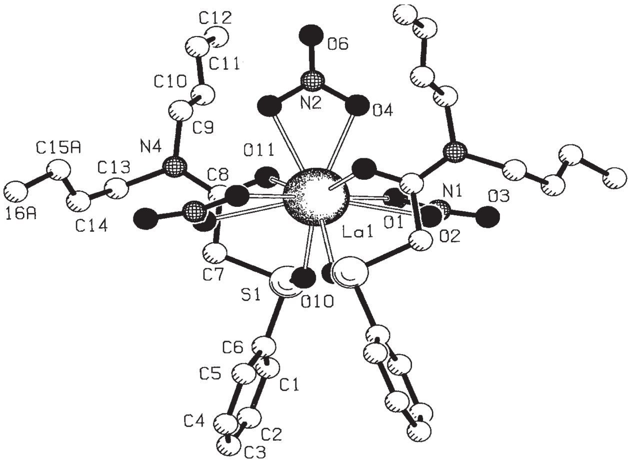

Fig. 1 Molecular structure of $[La(NO_3)_3(C_6H_5SOCH_2CON(C_4H_9)_2)_2]$.

The molecular structure of $[La(NO_3)_3(C_6H_5SOCH_2CON(C_4H_9)_2)_2]$ is shown in Fig. 1. and the selected inter atomic bond distances and angles are given in Table 1. The structure shows that $C_6H_5SOCH_2CON(C_4H_9)_2$ is bonded through both sulfoxo and carbamoyl oxygen atoms to the lanthanum (III) nitrate, and acts as a bidentate chelating ligand. Four oxygen atoms from two of the $C_6H_5SOCH_2CON(C_4H_9)_2$ ligands and six oxygen atoms from three of the nitrate groups give a distorted bi-capped square anti-prismatic geometry around the lanthanum (III) ion. The observed lanthanum to nitrato oxygen bond distances (2.606(3)–2.669(3) Å) are comparable in magnitude with those observed in $[La(NO_3)_3\{(C_2H_5)_2NCOCH_2CON(C_2H_5)_2\}_2]$[5c], $[La(NO_3)_3.(DMSO)_4]$,[5d] $[La(NO_3)_3(OPPh_3)_4]$[5e] and $[La(NO_3)_3(OPPh_2Me)_3]$.[5f]

The La–O(amide) (2.5684(18) Å) and La–O(sulfoxide) (2.479(2) Å) distances are closer to those values reported earlier for $[La(NO_3)_3\{(C_2H_5)_2NCOCH_2CON(C_2H_5)_2\}_2]$[5c] and $[La(NO_3)_3(DMSO)_4]$[5d] respectively. The whole molecule is stabilised in the solid state by various intra- and inter-molecular hydrogen bonding interactions to give a linear polymeric arrangement along the *c*-axis (see the supporting

Table 1 Selected inter atomic bond distances (Å) and angles (°) for the compound $[La(NO_3)_3(C_6H_5SOCH_2CON(C_4H_9)_2)_2]$

La1–O1	2. 669(3)	La1–O2	2. 617(2)	La1–O4	2. 606(3)
La1–O10	2. 479(2)	La1–O11	2. 5684(18)	S1–O10	1. 508(2)
S1–C6	1. 781(3)	S1–C7	1.806(3)		
O11–La1–O4	75.11(8)	O10–La1–O10	69. 20(9)		
O11–La1–O11	151.93(9)	O10–La1–O4	141.20(9)		
O10–La1–O2	86.77(9)	O10–La1–O4	136.29(9)		
O10–La1–O2	72.64(8)	O11–La1–O2	69.85(7)		
O11–La1–O2	116.68(7)	O10–La1–O4	141.20(9)		
O11–La1–O4	79.30(8)	O10–La1–O4	136.29(9)		

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Table 2 Crystal and structural refinement details for the compound $[La(NO_3)_3(C_6H_5SOCH_2CON(C_4H_9)_2)_2]$

Empirical formula	$C_{32}H_{50}N5O_{13}S_2La$
Formula weight	915 82
Crystal System	Monoclinic
Space Group	C2/c (No. 15)
A (Å)	18.4239 (17)
B (Å)	16.8708(15)
C (Å)	16.1944 (15)
β (°)	122.98 (1)
Volume (Å^3)	4222.1 (7)
Z (formula unit)	4
μ (Mo Kα) (mm)	1.173
Calculated density (g/cm^3)	1.441
2θ Range for data collection (°)	1.8 to 25. 0
Reflections collected/Unique/R(int)	10542/3713/0.019
Data/restraints/parameters	3713/0/260
Goodness of fit on F^2	0.69
Final R indices [I >2σ (I)]	0.0295
R indices (all data)	0.0891
Largest diff. Peak and hole (e Å^3)	0.68, –0.49

$W = 1/[\sigma^2(Fo^2) + (0.0513P)^2 + 5.\ 3717P]$; $P = (Fo^2 + 2Fc^2)/3$

information). These linear arrangements are arranged one-over-another along the *b*-axis direction to give a layered structure.

Experimental

Synthesis of $[La(NO_3)_3\{C_6H_5SOCH_2CON(^iC_3H_7)_2\}_2]$: A mixture of $[La(NO_3)_3.6H_2O]$ (500 mg, 1.15 mmol) and $C_6H_5SOCH_2CON(^iC_3H_7)_2$ (650 mg, 2.44 mmol) were refluxed in ethyl acetate for about 2 hours and the resulting white precipitate was filtered, washed with diethyl ether and dried. This product was recrystallised from CH_2Cl_2/hexane mixture as white crystalline solid (850 mg, 86% yield). Analysis calcd for $C_{28}H_{42}O_{13}S_2N_5La$: C, 39.1; H, 4.9; N, 8.1. Found: C, 40.2; H, 5.0; N, 7.7. IR (KBr, ν cm^{-1}): 1593 (CO); 1521, 1307,1274 (NO_3); 1041 (SO). ^1H NMR (CD_3OD, δ ppm): 1.16(d, 6 Hz,CH_3, $^iC_3H_7$); 1.17(d,6 Hz, CH_3, $^iC_3H_7$); 1.33(d,6 Hz, CH_3, $^iC_3H_7$); 1.38(d, 6 Hz, CH_3, $^iC_3H_7$); 3.6 (br, m, CH, $^iC_3H_7$); 4.88 (br, s, $SOCH_2$ CO); 7. 63(m, C_6H_5); 7. 82(m, C_6H_5).

Synthesis of $[La(NO_3)_3\{C_6H_5SOCH_2CON(C_4H_9)_2\}_2]$: This was prepared similar to the previous compound. Analysis calcd. $C_{32}H_{50}O_{13}S_2N_5La$: C, 41.9; H, 5.5; N, 7.6 Found: C, 42.2; H, 5.6; N, 7.7. IR (KBr, ν cm^{-1}): 1595 (CO); 1523,1307,1275 (NO_3); 991 (SO). ^1H NMR (CD_3OD, δ ppm): 0.9–1.0 (m, CH_3, Bu); 1.26–1.36 (m,CH_2, Bu); 1.45–1.53 (m, CH_2, Bu); 3.29–3.35 (m, NCH_2, Bu); 4.89 (s, OS-CH_2-CO); 7. 63–7.84 (m, C_6H_5).

Synthesis of $[La(NO_3)_3\{C_6H_5SOCH_2CON(^iC_4H_9)_2\}_2]$: This was prepared similar to the previous compound. Analysis calcd for $C_{32}H_{50}O_{13}S_2N_5La$: C, 41.9; H, 5.5; N, 7.6. Found: C, 42.1; H, 5.6; N, 7.8. IR (KBr, ν cm^{-1}): 1595 (CO); 1523,1307,1275 (NO_3); 991 (SO). ^1H NMR (CD_3OD, δ ppm): 0.9–1.0 (m, CH_3, Bu); 1.26–1.36 (m, CH_2, Bu); 1.45–1.53 (m,CH_2, Bu); 3.29–3.35 (m, NCH_2, Bu); 4.89 (s, OS-CH_2-CO); 7. 63–7.84 (m, C_6H_5).

X- ray crystallography: The X-ray diffraction data were collected on a Siemens SMART CCD diffractometer fitted with a graphite monochromated Mo–K_α radiation (λ = 0.71073 Å) at 297(2)°. The structure was solved by direct method, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2 using SHELXTL[6] version 5.1. One of the alkyl chains was disordered with two carbon atoms (C15 and C16) and these carbon atoms were refined over two sites. Apart from these atoms, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with geometrical constraints with ideal bond lengths and angles and were treated as riding atoms. A summary of crystallographic and refinement details is given in Table 2.

Received 20 August 2007; accepted 10 December 2007
Paper 07/4802 doi: 10.3184/030823407X268098

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