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Preparation, characterization and crystal structure of the complex formed between *N,N,N′,N′*-tetrabutylmalonamide and lanthanum(III) nitrate

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Abstract: The complex $[La(NO_3)_3(TBMA)_2]$ (TBMA = *N,N,N',N'*-tetrabutylmalonamide) was prepared by the extraction method and characterized by single-crystal X-ray diffraction. The complex consists of two bidentate TBMA extractant and three bidentate nitrate ions coordinated to a La^{3+} ion. The lanthanum(III) is 10-coordinate, being bonded to four oxygen atoms of the malonamides and six oxygen atoms of the three nitrates. The crystal data are as follows: $C_{38}H_{76}N_7O_{13}La$, M_r = 977.97, triclinic system, space group P_1, a = 1.3025(12), b = 1.4353(14), c = 0.4871(13) nm, α = 70.025(17), β = 71.411(19), γ = 84.017(18)º, V = 2.476(4) nm^3, Z = 2, F(000) = 1028, D = 1.312 g.cm^{-3}, R_1 = 0.0833, wR_2 = 0.1471.

Keywords: complex, *N,N,N',N'*-tetrabutylmalonamide, lanthanum(III) nitrate, crystal structure.

INTRODUCTION

There has been significant interest in recent years in the study of new extractants,[1,2] especially alkyl-substituted amides as alternative extractants to organophosphorus compounds for nuclear fuel reprocessing. Numerous studies have been conducted on the solvent extraction of actinides and lanthanides by monoamides[3–8] and diamides.[9–17] While most of these were focused only on the determination of distribution, a few papers provide information aimed at understanding the effect of the ligand structure on the metal extraction. Clement[18] performed an exhaustive survey of crystal structure data on simple amides and metal complexes containing monodentate amide ligands and discrussed the orientational preference of the coordinated amide ligands in terms of the M–O–C bond angles and M–O–C–N torsin angles. In numerous papers, the coordination complexes of various malonamide derivatives were described, such as $[UO_2(TBMA)(NO_3)_2]$,[19] $[Nd(NO_3)_3(TEMA)_2]$ (TEMA = *N,N,N',N'*-tetraethylmalonamide),[20] $[Yb(NO_3)_3(TEMA)_2]$,[20]

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$[La(NO_3)_3(TEMA)_2]$,[21,22] $[La(NO_3)_3(TEEEMA)_2]$ (TEEEMA = 2-(2-ethoxyethyl)-*N,N,N',N'*-tetraethylmalonamide),[23] $[Ln(NO_3)_3(L)_2]$ (Ln = Nd or Pr, L = butyl-*N,N'*-dimethyl-*N,N'*-diphenyl malonamide and ethoxyethyl-*N,N'*-dimethyl-*N,N'*-diphenyl malonamide)[24] and $[UO_2(TMMA)(NO_3)_2]$,[25] in which the nitrates and ligands are both bidentate.

The extraction behavior of TBMA for f-block elements in different diluents have been investigated.[16,17,26,27] However, to the best of our knowledge, no crystal structure of coordination complex of TBMA with lanthanides has hitherto been reported. TMMA and TEMA cannot be used as extractants due to their small alkyl substituent and can be regard only as model ligands similar to TBMA used in actual extraction processes. The study of the structure of TBMA complexes would provide more precise information for understanding the extractant structure-extractability relationship. In the present paper, the preparation and the crystal structure of $[La(NO_3)_3(TBMA)_2]$ are reported.

EXPERIMENTAL

Measurements and the methods applied

General materials and methods: TBMA was synthesized experimentally as described elsewhere.[26] The other reagents were of AR grade.

The IR spectra were recorded on a Bio-Rad FTS-165 spectrometer. Each spectrum was accumulated over 60 scans at a resolution of 2 cm^{-1}, using air as the background. Elemental analysis was performed using a Perkin–Elmer 24000 II elemental analyzer. The melting point measurement was carried out using a XT4 melting point apparatus. The electronic spectra were recorded on a UV-3000 spectrophotometer.

Preparation of $[La(NO_3)_3(TBMA)_2]$: Equal volumes of 0.50 mol cm^{-3} TBMA in toluene and aqueous phases containing 0.10 mol cm^{-3} $La(NO_3)_3$ and 10 mol dm^{-3} $LiNO_3$ were agitated for 40 min (enough for equilibrium) at 25 ºC. The two phases were then centrifuged and assayed and the aqueous phase was taken out. Fresh aqueous phase was added to the equlibrated organic phase and the foregoing procedure was repeated three times. The organic phase was carefully taken out and slowly evaporated to dryness. The resulting product was recrystallized from *n*-hexane twice to yield colourless acerous crystals. The crystals were dissolved in toluene and slow evaporated thus yielded colorless single crystals suitable for X-ray crystallography. The complex is soluble in aromatic hydrocarbon, dimethylsulfoxide and *N,N*-dimethylformamide, although only slightly soluble in aliphatic hydrocarbons.

$[La(NO_3)_3(TBMA)_2]$, mp. 138–139 ºC; FTIR ν(cm^{-1}, KBr): 733.65(*m*), 819.35(*w*), 938.7(*w*), 1026.51(*w*), 1038.10(*w*), 1286.88(*s*), 1300.68(*s*), 1382.86(*s*), 1460.89(*s*), 1577.9(*s*), 1608.45(*s*), 2871.26(*s*), 2933.17(*s*), 2957.96(*s*); UV/VIS λ(nm, in hexane): 275 (277 for TBMA); Anal. for $C_{38}H_{76}N_7O_{13}La$: C 46.63, H 7.77, N 10.02; found: C 46.65, H 7.75, N 9.97.

X-Ray crystallography: Crystallographic data ($1.51 < \theta < 25.03$) for $La(NO_3)_3(TBMA)_2$ were collected on a Bruker Smart-1000 CCD area detector using Mo K*a* (λ = 0.071073 nm) radiation. The crystal structure was solved using the SHELXL-97 software package. Table I summarizes the data collection parameters. All non-hydrogen atoms were anisotropically refined. The positions of the hydrogen atoms were calculated. The thermal parameters were assigned based on the carbon atom to which the H-atoms are bonded.

CCDC reference number 231277.

TABLE I. Crystallograhic parameters for $[La(NO_3)_3(TBMA)_2]$

Empirical formula	$C_{38}H_{76}N_7O_{13}La$
Formula weight	977.97
Crystal size/mm	0.38×0.18×0.15
Temperature/K	298(2)
Crystal system	Triclinic
Space group	P_1
a/nm	1.3025(12)
b/nm	1.4353(14)
c/nm	0.4871(13)
α/º	70.025(17)
β/º	71.411(19)
γ/º	84.017(18)
V/nm^3	2.476(4)
Z	2
D/g cm^{-3}(Calculated)	1.312
F(000)	1028
θ range/º	1.51 to 25.03
Reflections collected	12423
Independent reflections	8477
Goodness of fit on F^2	0.726
$R1$	0.0833
$wR2$	0.1471
Largest diff peak and hole/(± 10^2 e nm^{-3})	7.74 – 8.37

RESULTS AND DISCUSSION

Fig. 1 shows the molecular structue of $La(NO_3)_3(TBMA)_2$, which is different from the stoichiometry of the extracted species, $La(NO_3)_3(TBMA)_3$, obtained in our extraction study in which the initial concentations of TBMA and La^{3+} were controlled at 0.50 and 5.00×10^{-3} mol dm^{-3}, respectively. Table II presents the key bond lengths and Table III shows selected bond angles. Although a number of crystal structure have been reported for lanthanide(III)–malonamide complexes,[20–24] this is the first crystal structure reported for a lanthanide(III)–TBMA complex. This structure is similar to that of TEMA, but there are some differences.

Fig. 1 shows that La(III) in the complex is ten-coordinate, being bonded to two bidentate TBMA extractants and three bidentate nitrate ions. In this ten-coordinate structure, the geometry can be best described in terms of a dodecahedron. The La^{3+}– O(TBMA) bond lengths are shorter (mean value 2.477 Å) than those of La^{3+} – O(nitrate) (mean value 2.531 Å). However, the mean values of the La^{3+}– O(TEMA)

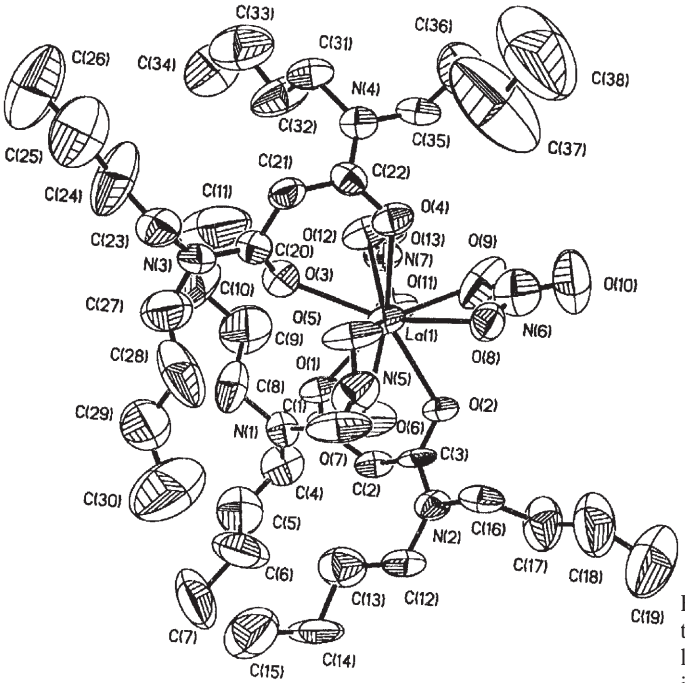

Fig. 1. Perspective view of the $[La(NO_3)_3(TBMA)_2]$ molecule with thermal ellipsoids drawn at the 50 % level.

and La^{3+}– O (nitrate) bond lengths are 2.50(2) and 2.623 Å, respectively.[21,22] It seems that the larger alkyl substituents of TBMA do not cause a bigger steric hindrance.

TABLE II. Selected bond lenghts Å, for $[La(NO_3)_3(TBMA)_2]$

La(1)–O(9)	2.312(16)	O(1)–C(1)	1.281(14)
La(1)–O(1)	2.447(9)	O(2)–C(3)	1.216(12)
La(1)–O(4)	2.458(8)	O(3)–C(20)	1.260(13)
La(1)–O(3)	2.480(9)	O(4)–C(22)	1.267(14)
La(1)–O(8)	2.488(9)	C(1)–C(2)	1.473(15)
La(1)–O(2)	2.518(7)	C(2)–C(3)	1.466(15)
La(1)–O(12)	2.578(9)	N(2)–C(3)	1.312(14)
La(1)–O(11)	2.594(8)	N(2)–C(12)	1.416(13)
La(1)–O(6)	2.621(10)	N(2)–C(16)	1.488(13)
La(1)–O(5)	2.633(9)	N(3)–C(20)	1.270(14)
La(1)–N(6)	2.894(13)	N(3)–C(23)	1.432(15)
La(1)–N(5)	3.031(15)	N(3)–C(27)	1.48(2)
N(1)–C(1)	1.278(13)	N(4)–C(22)	1.327(15)
N(1) –C(4)	1.414(16)	N(4) –C(35)	1.451(15)
N(1) –C(8)	1.524(15)	N(4) –C(31)	1.485(15)

TABLE III. Selected bond angles º for [$La(NO_3)_3(TBMA)_2$]

O(6)–La(1)–O(5)	45.4(3)	O(9)–La(1)–O(12)	75.5(4)
O(1)–La(1)–O(3)	74.4(3)	O(8)–La(1)–O(12)	119.4(4)
O(1)–La(1)–O(4)	145.0(3)	C(3)–O(2)–La(1)	123.3(7)
O(4)–La(1)–O(2)	147.9(3)	C(20)–O(3)–La(1)	132.2(10)
O(3)–La(1)–O(2)	141.3(3)	C(22)–O(4)–La(1)	123.2(8)
O(4)–La(1)–O(3)	70.6(3)	C(1)–N(1)–C(4)	126.1(13)
O(9)–La(1)–O(8)	49.4(4)	C(1)–N(1)–C(8)	119.7(12)
O(1)–La(1)–O(2)	67.2(2)	C(4)–N(1)–C(8)	114.1(12)
O(12)–La(1)–O(11)	46.7(3)	C(3)–N(2)–C(12)	126.7(13)
O(9)–N(6)–O(10)	137.6(18)	C(3)–N(2)–C(16)	119.4(13)
O(9)–N(6)–O(8)	108.7(12)	C(12)–N(2)–C(16)	113.5(11)
O(10)–N(6)–O(8)	113.7(16)	O(5)–N(5)–O(6)	117.8(14)
O(13)–N(7)–O(12)	124.8(16)	O(5)–N(5)–O(7)	122.3(18)
O(13)–N(7)–O(11)	121.6(17)	O(6)–N(5)–O(7)	119.1(18)
O(12)–N(7)–O(11)	113.2(12)	N(2)–C(3)–C(2)	120.2(13)
N(1)–C(1)–O(1)	121.3(14)	C(3)–C(2)–C(1)	113.3(11)
N(1)–C(1)–C(2)	120.6(13)	O(2)–C(3)–N(2)	120.2(16)
O(1)–C(1)–C(2)	117.8(13)	O(2)–C(3)–C(2)	119.7(11)
C(1)–O(1)–La(1)	140.1(8)		

The configuration of the malonamide was studied. The geometry of the malonamide molecules can be characterized by O … O distances and the values of the torsion angles. The mean values of the O … O distances in the TEMA moieties are 2.80(5) and 2.80(4) Å[21] and 2.80(1) Å for TBMA. The O=C … C=O torsion angles indicate that, in TEMA the central parts are more planar, with values as low as 15.0 and 22.8º, than TBMA in $La(NO_3)_3(TBMA)_2$, in which the values of the torsion angles are –42.35 and –46º, respectively. Further study on the structure of $La(NO_3)_3(TBMA)_2$ indicates that the angles of O(1)–C(1)–C(2) and O(3)–C(20)–(21), are 117.9 and 118.7º, respectively, being smaller than the normal values (120º for sp^2 hydridization of the C atomic orbital). The smaller angles probably suggest that the O … O distances do not increase with increasing O=C … C=O torsion angle.

Or particular significance is the planarity of functional groups of the TBMA moieties. For example, in Fig. 1, the atoms, O(1), C(1), C(2), N(1), C(8) and C(4) are almost in one plane. As it is known, the nitrogen atom in a trialkyl amine is sp^3 hybridized and the C … N … C angles are about 109 º. However, the three bonds around the nitrogen are almost planar and the sum of the nitrogen bond angles is about 360º in the structure of $La(NO_3)_3(TBMA)_2$, which is consistent with sp^2 hybridization. It is suggested that p-π conjugation between π bond of the C=O group and the non-hybridized p orbital of the attached nitrogen atom occurs in the amide molecules, which results in

the planarity of the hard core of TBMA. The bond between the nitrogen atom and the carbonyl cannot rotate freely due to the p-π conjugation.

CONCLUSION

In this paper, the crystal structure of $[La(NO_3)_3(TBMA)_2]$ is described. La(III) in the complex is ten-coordinate, being bonded to two bidentate TBMA extractants and three bidentate nitrate ions. The p-π conjugation, which occurred between the π bond of the C=O group and the non-hybridized p orbital of the attached nitrogen atom, results in the planarity of the functional groups of the TBMA moieties.

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ИЗВОД

ДОБИЈАЊЕ, КАРАКТЕРИЗАЦИЈА И КРИСТАЛНА СТРУКТУРА КОМПЛЕКСА КОЈИ СЕ ГРАДИ ОД *N,N,N',N'*-ТЕТРАБУТИЛМАЛОНАМИДА И ЛАНТАН(III) НИТРАТА

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Комплекс $[La(NO_3)_3(TBMA)_2]$ (TBMA = *N,N,N',N'*-тетрабутилмалонамид) је направљен методом екстракције и окарактерисан X-рендгенском дифракцијом на монокристалу. Комплекс се састоји од два бидентатна екстрактанта TMBA и три бидентатна нитратна јона коорионована за La^{3+} јон. Лантан(III) је 10-координован, везујући се за четири кисеоникова атома малонамида и шест кисеоникових атома за три нитратна јона. Кристални подаци су следећи: $C_{38}H_{76}N_7O_{13}La$, M_r = 977.97, триклинични систем, просторна група P_1, a = 1.3025(12), b = 1.4353(14), c = 0.4871(13) nm, α = 70.025(17), β = 71.411(19), γ = 84.017(18)°. V = 2.476(4) nm^3, Z = 2, F(000) = 1028, D = 1.312 g cm^{-3}, R_1 = 0.0833, wR_2 = 0.1471.

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