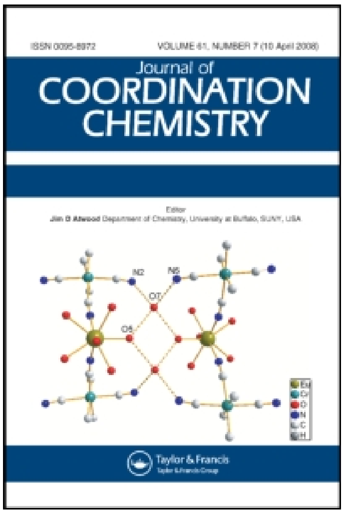
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Characterization of Complexes of Lanthanide Perchlorates with *N,N,N',N'*-Tetraphenyl-3,6-Dioxaoctanedioicdiamide

Liu Weisheng[a]; Tan Minyu[a]; Jiao Tianquan[a]; Tan Ganzu[b]
[a] Department of Chemistry, Lanzhou University, Lanzhou, PR China [b] Lanzhou Institute of Chemical Physics, Academia Sinica, PR China

To cite this Article Weisheng, Liu , Minyu, Tan , Tianquan, Jiao and Ganzu, Tan(1992) 'Synthesis and Characterization of Complexes of Lanthanide Perchlorates with *N,N,N',N'*-Tetraphenyl-3,6-Dioxaoctanedioicdiamide', Journal of Coordination Chemistry, 26: 2, 155 — 160

To link to this Article: DOI: 10.1080/00958979209407925

URL: http://dx.doi.org/10.1080/00958979209407925

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem. 1992, Vol. 26. pp. 155–160
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF LANTHANIDE PERCHLORATES WITH *N,N,N′,N′*-TETRAPHENYL-3,6-DIOXAOCTANEDIOICDIAMIDE

LIU WEISHENG, TAN MINYU*, JIAO TIANQUAN
Department of Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

and TAN GANZU
Lanzhou Institute of Chemical Physics, Academia Sinica, P.R. China

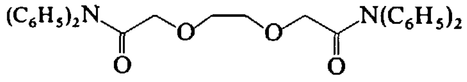
(*Received 13 December 1991; in final form 10 January 1992*)

Lanthanide perchlorate complexes with the ligand *N,N,N′,N′*-tetraphenyl-3,6-dioxaoctanedioicdiamide: $[Ln(L)_2(H_2O)_n](ClO_4)_3$ (where n = 2 for Ln = La, Pr, Nd; n = 1 for Ln = Sm-Tb) have been prepared by reaction of the corresponding lanthanide perchlorate with the ligand and characterized by elemental analysis, conductivity measurements, IR, electronic and ^1H NMR spectra and TG-DTA techniques. In all complexes, the ligand shows tetradentate behaviour.

Keywords: Non-cyclic polyether, lanthanide perchlorates, complexes

INTRODUCTION

Macrocyclic polyethers, so-called crown ethers, show a high complexation selectivity which makes them adequate reagents for investigations of separations of lanthanide ions.[1] On the other hand, non-cyclic polyethers, the open-chain analogues of crown ethers,[2] can be used in extraction and analysis (ion-selective electrodes) of the rare earths.[3–5] The use of these complexes as spectroscopic probes of complex materials will probably attract increasing attention.[1] Ding *et al.* have reported the extraction of lighter lanthanide ions with five derivatives of glycol-*O,O′*-diacetamides,[4] among which *N,N,N′,N′*-tetraphenyl-3,6-dioxaoctanedioicdiamide has the largest separation factor. In the molecule there are four oxygen atoms available for complexation. In order to investigate the coordinating power of this ligand towards rate earth ions, we report the preparation and characterization of lanthanide perchlorate complexes with the ligand.



N,N,N′,N′-Tetraphenyl-3,6-dioxaoctanedioicdiamide (L)

---

* Author for correspondence.

EXPERIMENTAL

Reagents

Lanthanide perchlorates were obtained by dissolving the corresponding oxides (99.95%) in 30% perchloric acid. The ligand was prepared according to the literature method.[6] All other chemicals were of AR grade and used without further purification.

Chemical and physical measurements

The metal ion was determined by EDTA titration using xylenol-orange as indicator. Carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyser. Conductivity measurements were carried out with a DDS-11A type conductivity bridge using 10^{-3} mol dm^{-3} solutions in acetonitrile at 25°C. The IR spectra were recorded on a Nicolet 170 SX FT-IR instrument using KBr discs in the 4000–250 cm^{-1} region. Thermal analyses (TG and DTA) were performed on a Beijing PCD-2 thermobalance using about a 10 mg powder sample at a heating rate of 10°C min^{-1} in static air. Electronic spectra were recorded with a Beckmann, Model DU-7, spectrophotometer in acetonitrile solutions. ^{1}H NMR spectra were measured on an FT-80A spectrometer in DMSO-d_6 solutions with TMS as internal standard.

Preparation of the complexes

Lanthanide perchlorate (0.3 mmol) and the ligand (0.6 mmol) were dissolved in 40 cm^3 of 1:1 (v/v) chloroform-methanol. After being stirred for 24 h the solution was allowed to evaporate to dryness. The residual solid obtained was dissolved in 20 cm^3 acetonitrile and then the solution was filtered. To the filtrate was added 80 cm^3 of ether with stirring so that the complex precipitated. The produce was isolated by filtration, washed with ether and dried *in vacuo* over P_4O_{10} for 48 h. All the complexes are powders with the characteristic colour of the corresponding lanthanide ion. Yield 80–85%.

RESULTS AND DISCUSSION

Analytical results are summarized in Table I. The analytical data indicate that all of these complexes conform to a 1:2 metal-to-ligand stoichiometry.

TABLE I
Analytical and molar conductance data for the complexes.

	Found (calc.)%				
Complex	C	H	N	Ln	Λm (s cm^2 mol^{-1})
$La(L)_2(ClO_4)_3.2H_2O$	50.28(50.24)	4.25(4.22)	4.01(3.91)	9.77(9.68)	350
$Pr(L)_2(ClO_4)_3.2H_2O$	50.39(50.17)	4.11(4.21)	3.92(3.90)	9.68(9.81)	347
$Nd(L)_2(ClO_4)_3.2H_2O$	50.31(50.05)	4.17(4.20)	3.88(3.89)	9.91(10.02)	348
$Sm(L)_2(ClO_4)_3.H_2O$	50.42(50.47)	4.01(4.09)	3.79(3.92)	10.46(10.53)	341
$Eu(L)_2(ClO_4)_3.H_2O$	50.32(50.41)	4.16(4.09)	3.98(3.92)	10.71(10.63)	348
$Gd(L)_2(ClO_4)^3.H_2O$	50.35(50.23)	4.00(4.08)	3.72(3.91)	10.82(10.96)	337
$Tb(L)_2(ClO_4)_3.H_2O$	50.06(50.17)	4.12(4.07)	3.97(3.90)	11.32(11.06)	342

TABLE II
Characteristic IR bands for the complexes (cm^{-1}).

Compound	$\nu(C{=}O)$	$\nu_{as}(C{-}O{-}C)$ $+\nu_3(ClO_4)$	$\nu_s(C{-}O{-}C)$	$\nu_4(ClO_4)$	$\nu(OH)$	$\rho_r(H_2O)$
L	1685 vs	1131s[a]	951 m			
$La(L)_2(ClO_4)_3.2H_2O$	1630 vs	1079–1120[b]	925 m	623 s	3380 m, b	601 m
$Pr(L)_2(ClO_4)_3.2H_2O$	1628 vs	1060–1120[b]	924 m	625 s	3356 m, b	602 w
$Nd(L)_2(ClO_4)_3.2H_2O$	1629 vs	1084–1120[b]	925 m	627 s	3334 m, b	597 w
$Sm(L)_2(ClO_4)_3.H_2O$	1631 vs	1092–1114[b]	924 m	625 s	3328 m, b	607 w
$Eu(L)_2(ClO_4)_3.H_2O$	1618 vs	1090–1115[b]	923 m	623 s	3332 m, b	605 w
$Gd(L)_2(ClO_4)_3.H_2O$	1630 vs	1086–1116[b]	925 m	624 s	3371 m, b	606 m
$Tb(L)_2(ClO_4)_3.H_2O$	1629 vs	1094–1120[b]	924 m	625 s	3358 m, b	608 w

[a] $\nu_{as}(C{-}O{-}C)$. [b] Broad band with several maxima.

All complexes are hygroscopic. They are soluble in DMSO, acetone and acetonitrile, slightly soluble in ethanol, nitromethane and chloroform, and sparingly soluble in benzene, ether and cyclohexane. The molar conductance values of the complexes in acetonitrile (Table I) indicate that all complexes act as 1:3 electrolytes,[7] implying that all the perchlorate groups are ionic.

IR spectra

Characteristic IR bands are collected in Table II. The ligand has $\nu(C{=}O)$ at $1685\,cm^{-1}$. This band appears at $1628–1631\,cm^{-1}$ in the spectra of the complexes with a shift of $54–57\,cm^{-1}$ to the lower frequency region thus indicating the C=O groups are coordinated to the metal ions. The IR spectrum of the ligand shows two bands at 951 and $1131\,cm^{-1}$ which may be assigned to $\nu_s(C{-}O{-}C)$ and $\nu_{as}(C{-}O{-}C)$, respectively. In the complexes, $\nu_{as}(C{-}O{-}C)$ strongly interferes with $\nu_3(ClO_4^-)$; the other $\nu_s(C{-}O{-}C)$ band is displaced by $26–28\,cm^{-1}$ towards lower wavenumbers suggesting that the ether oxygen atoms also take part in coordination to the metal ions. The ligand, therefore, acts as a tetradentate, forming a ring-like structure similar to that in (triethyleneglycol)trinitrolanthanide.[8,9]

The $\nu(OH)$ and $\rho_r(H_2O)$ modes of coordinated water appear at 3328–3380 and $597–608\,cm^{-1}$, respectively, in the spectra of all complexes.[10] The perchlorate groups of the complexes have two IR active modes only; ν_3 and ν_4 appear at ~1100 and ~$625\,cm^{-1}$, respectively. This also indicates the presence of ionic perchlorate groups.[11]

Thermal analyses

Thermal analysis data are summarized in Table III.

TG and DTA curves for the ligand show that the compound initially melts at 147°C and then decomposes from 250 to 610°C, producing two exothermic peaks at 373 and 563°C. All complexes show similar patterns of decomposition with three weight losses. The first occurs at 112–120°C corresponding to the loss of two water molecules for lighter lanthanides (La, Pr, Nd) or one water for middle lanthanides (Sm–Tb). The weight losses compare favourably with theoretical values (Table III).

TABLE III
Thermal analysis data for the ligand and complexes.

Compound	Endothermic process		Exothermic process	
	DTA peak (°C)	Weight loss (%)[a]	DTA peak (°c)	
L	147[b]		373	563
$La(L)_2(ClO_4)_3.2H_2O$	112	3.62(2.51)	283	520
$Pr(L)_2(ClO_4)_3.2H_2O$	115	2.75(2.51)	286	506
$Nd(L)_2(ClO_4)_3.2H_2O$	120	2.91(2.50)	290	497
$Sm(L)_2(ClO_4)_3.H_2O$	116	1.44(1.26)	296	514
$Eu(L)_2(ClO_4)_3.H_2O$	115	1.90(1.26)	298	521
$Gd(L)_2(ClO_4)_3.H_2O$	109	1.81(1.26)	304	515
$Tb(L)_2(ClO_4)_3.H_2O$	112	1.87(1.25)	307	526

[a] Calculated values in parentheses. [b] Melting point.

Moreover, the relatively high temperatures of dehydration are consistent with the presence of coordinate water (as inferred from the IR data). The dehydrated complexes decompose very rapidly, producing an exothermic peak in the 283–307°C range. Subsequently another exothermic peak and continuous weight loss was detected to 800°C. At this temperature Ln_2O_3 (Pr_6O_{11} for the praseodymium complex; Tb_4O_7 for the terbium complex) is formed.

Electronic spectra

The electronic spectra in the visible region of the Pr(III), Nd(III) and Sm(III) complexes exhibit alternations in intensity and shifts in position of the absorption bands relative to the corresponding Ln(III) aquoions.[12] The shift has been attributed by Jørgensen[13] to the effect of crystal fields upon inter-electronic repulsion between the 4f electrons, and is related to covalance in the metal-ligand bond, assessed by Sinha's parameter (δ), naphelauxetic ratio (β), and the bonding parameter ($b^{1/2}$).[14–16] These covalent parameters for the Pr(III), Nd(III) and Sm(III) complexes are given in Table IV.

The values of β, which are less than unity, and positive values of δ and $b^{1/2}$ support the existence of partial covalent bonding between metal and ligand.[17] The magnitudes of covalency and bonding parameters increase from Pr(III) to Sm(III), indicating that the extent of the covalent character of the metal-ligand bond increases with increase in atomic number (in conformity with lanthanide contraction).

^1H NMR spectra

^1H NMR spectra of the lanthanide complexes are obviously different due to the different number of unpaired 4f electrons and the different magnetism of the lanthanide ions. The La(III) ($4f^0$) and the Sm(III) ($4f^5$) complexes exhibit a sharp and strong spectrum, and a broad and weak spectrum, respectively, while with the Gd(III) ($4f^7$) complex no signal was observed. The latter case may be due to a combination of large shifts and extensive broadening of the signals,[18] since the Gd(III) ion has the maximum number of unpaired electrons and is therefore strongly paramagnetic.

TABLE IV
Covalence parameters for some of the complexes.

Complex	β	δ	$b^{1/2}$
$Pr(L)_2(ClO_4)_3.2H_2O$	0.9981	0.1904	0.0308
$Nd(L)_2(ClO_4)_3.2H_2O$	0.9966	0.3412	0.0412
$Sm(L)_2(ClO_4)_3.H_2O$	0.9950	0.5025	0.0500

TABLE V
^1H NMR spectral data for the ligand and some of the complexes (chemical shifts in ppm, from TMS).

Compound	$\delta(C_6H_5-)$	$\delta(-\overset{\overset{O}{\|}}{C}CH_2-)$	$\delta(-C_2H_4-)$	$\delta(H_2O)$
L	7.37(s, 2OH)	4.01(s, 4H)	3.57(s, 4H)	
$La(L)_2(ClO_4)_3.2H_2O$	7.49(s, 4OH)	4.53(s, 8H)	3.89(s,8H)	2.88(s,4H)
$Sm(L)_2(ClO_4)_3.H_2O$	7.50(s, 4OH)	4.55(s, 8H)	3.91(s, 8H)	2.76(s, 2H)

Table V shows ^1H NMR data for the ligand and the La(III) and Sm(III) complexes. The spectrum of the ligand exhibits three singlets at 7.37, 4.01 and 3.57 ppm, assigned to C_6H_5-, $-\overset{\overset{O}{\|}}{C}CH_2-$ and $-C_2H_4-$ protons, respectively. Upon coordination all the ligand proton signals move to lower field, among which $-\overset{\overset{O}{\|}}{C}CH_2-$ and $-C_2H_4-$ protons shift by some 0.32–0.54 ppm, while C_6H_5- protons shift 0.12–0.13 ppm. This is due to the inductive effect of Ln(III) ions in the complexes. The proton signals of the water molecules in the complexes are observed at 2.76–2.88 ppm. In the ^1H NMR spectra of the complexes, the ratios of integrated intensities are in good agreement with elemental analyses.

CONCLUSION

The open-chain analogue of crown ethers, *N*,*N*,*N*′,*N*′-tetraphenyl-3,6-dioxaoctanedioicdiamide can react with lanthanide perchlorates in nonaqueous medium to form stable solid complexes, which may be formulated as $[Ln(L)_2(H_2O)_n](ClO_4)_3$ (where $n=2$ for Ln = La, Pr, Nd, and 1 for Ln = Sm-Tb). The ligand acts as a tetradentate, forming a ring-like structure. Similar structures were also found for lanthanide complexes with other noncyclic polyethers.[8,9]

REFERENCES

1. J.-C.G. Bünzli and D. Wessner, *Coord. Chem. Rev.*, **60**, 191 (1984).
2. J.-C.G. Bünzli, J.-M. Pfefferlé, B. Ammann, G. Chapuis and F.-J. Zuniga, *Helv. Chim. Acta.*, **67**, 1121 (1984).

3. Yang Yusheng and Ding Yuzhen, *J. Nucl. Radiochem.*, **4**, 21 (1982).
4. Ding Yuzhen, Lu Jiachun, Yang Yusheng, Tan Ganzu and Xu Junzhe, *Huaxue Shiji*, **8**, 201 (1986).
5. Yang Yansheng and Cai Shaohua, *Huaxue Shiji*, **6**, 133 (1985).
6. Tan Ganzu, Xu Junzhe, Yiao Zhongqi and Zhang Fusheng, *Huaxue Shiji*, **5**, 100 (1983).
7. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. Y. Hirashima, T. Tsutsui and J. Shiokowa, *Chem. Let.*, 1405 (1982).
9. Y. Hirashima, K. Kanetsuki and I. Yonezu, *Bull. Chem. Soc. Jpn.*, **56**, 738 (1983).
10. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley, New York, 1978), 3rd Edn., p. 227.
11. J.-C.G. Bünzli, H.T. Oanh and B. Gillet, *Inorg. Chim. Acta*, **53**, L219 (1981).
12. W.T. Carnall, P.R. Fields and K. Kajnak, *J. Chem. Phys.*, **49**, 4412 (1968).
13. C.K. Jørgensen, *Acta Chem. Scand.*, **11**, 1981 (1957).
14. C.K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).
15. S.P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).
16. D.E. Henrie and G. R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).
17. A.K. Solanki and A. M. Bhandaka, *J. Inorg. Nucl. Chem.*, **41**, 1311 (1979).
18. E.C. Okafor, *J. Inorg. Nucl. Chem.*, **42**, 1155 (1980).