Synthesis and Characterization of Complexes of Lanthanide Perchlorate with DDO

Yan-Bo Wang and Yan Shi

ABSTRACT

The complexes of lanthanide perchlorates in conjunction with N,N'-diethyl-N,N'-diphenyl-3-oxapatanediamide (DDO) ligand have been prepared in non-aqueous media. These complexes with general formulation [Ln(DDO)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ (Ln = La, Pr, Nd, Sm, Eu) have been characterized by elemental analysis, conductivity measurement, IR spectra, $^1$H NMR spectra and TG-DTA techniques. In all the complexes, the ligand (DDO) shows tridentate behavior.

INTRODUCTION

The open-chain crown ethers were pioneer studied and developed by Simon [1] and Vögtle [2] in the 1970s, their structures abound change. This kind of easily prepared compounds, low-toxicity or nontoxic [3], can selectively complex with metal ions and be widely used in extraction separation [4] of lanthanide, actinide and alkali metal elements [5]. As a result, the study and research for open-chain crown ethers and their analogues has attracted much attention of scientists. Previous study has demonstrated that rare earth elements have many physiological functions [6], and a few of them have been found in clinical medication. Due to important theoretical significance and practical application of open-chain crown ether, we have been kept on our research of the coordination performance of the open-chain crown ether with rare earth elements for many years [7]. In this report, we are investigating lanthanide perchlorate complexes of DDO.

Wang Yan-bo$^{1,a}$ and Shi Yan$^{1,b}$

$^1$Tianshui Normal University, College of Chemical Engineering and Technology, Tianshui 741001 Tianshui P.R. China.

$^a$tswangyb@sina.com, $^b$shiyan641122@sohu.com
EXPERIMENT

Chemicals

All agents and solvents are analytically pure and anhydrous. Lanthanide perchlorate were obtained by dissolving the corresponding oxide in perchloric acid (6 mol/L), and dried in vacuum over P$_2$O$_5$ for 48h. All other chemicals were AR grade and used without further purification. The ligand (DDO: C$_{20}$H$_{24}$N$_2$O$_3$, mp: 96-97ºC, IR(cm$^{-1}$):1672, 1159, 948cm$^{-1}$, $^1$H NMR(δppm):7.37, 3.95, 3.72, 1.10 was prepared according in literature [8], its structure is shown in Fig. 1.

Equipment

The metal ions were determined by EDTA titration using xylenol orange as indicator. Carbon, nitrogen and hydrogen were determined using a Vario elemental analyzer. Conductivity measurements were carried out with a DDS-11A type conductivity bridge using 10$^{-3}$mol⋅L$^{-1}$ solutions in acetonitrile at 25ºC. The IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer using KBr discs in the 4 000~250 cm$^{-1}$ region. $^1$H NMR spectra were measured on a Nicolet FT-80A spectrometer in DMSO-d$_6$ solution with TMS as internal standard. Thermal analyses (TG-DTA) were performed on a Beijing PCD-2 thermobalance using about 10×10$^{-3}$ g powdered sample and working at a heating rate of 5ºC/min in static air. Melting point was determined by Shanghai X-4 melt apparatus and the thermometer was not emended.

Preparation of the Complexes

A solution of lanthanide perchlorate (0.3 mmol) and DDO (0.6 mmol) in chloroform-methanol (1:1 v/v, 30 mL) was stirred at room temperature for 24h, then a solid was obtained by partially evaporating solvent of the reaction with a rotated evaporator. The solid was dissolved in anhydrous acetonitrile (30 mL), then anhydrous ether (about 100 mL) was added drop-wise to the solution, the lanthanide perchlorate complexes of DDQ was obtained. The precipitated complex was filtered, washed with anhydrous ether (10mL×3), and then dried in vacuum over P$_2$O$_5$ for about one week. All the complexes are hygroscopic powder solid with the characteristic color of corresponding lanthanide ion.

RESULTS AND DISCUSSION

The metal ion was determined by EDTA titration using xylenol orange as an indicator. The melt point and element analysis of these complexes are given in Table 1. The found values approached the calculate values. The element analysis values showed that the chemical composition of these complexes is: LnClO$_3$·2DDO·2H$_2$O (Ln = La ~ Eu, except Pm ). They are easily soluble in DMSO, DMF, acetonitrile, methanol and ethanol and partially soluble in benzene, ether and cyclohexane. The molar conductance values of these complexes (Am): 368-387s⋅cm$^2$⋅mol$^{-1}$ (in acetonitrile, 25ºC) indicate that the complexes act as 1:3 electrolytes$^{[9]}$ and all three ClO$_4^-$ ions are ionizible. Their metal points are higher, and increase with the decrease of the radii.
Table 1. Analytical And Molar Conductance Data For The Complexes.

| Compounds                  | m.p. (ºC) | Found (calc.)% | Λm (s cm² mol⁻¹) |
|----------------------------|-----------|----------------|------------------|
| [La DDO₂(H₂O)₂] (ClO₄)₃  | 185~187   | 41.61(41.63)   | 4.56(4.54)       | 4.87(4.85)       | 12.12(12.08)     | 368   |
| [Pr DDO₂(H₂O)₂] (ClO₄)₃  | 191~192   | 41.53(41.56)   | 4.55(4.53)       | 4.86(4.85)       | 12.23(12.19)     | 371   |
| [NdDDO₂(H₂O)₂] (ClO₄)₃   | 195~196   | 41.43(41.44)   | 4.54(4.52)       | 4.86(4.83)       | 12.41(12.44)     | 374   |
| [SmDDO₂(H₂O)₂] (ClO₄)₃   | 202~203   | 41.18(41.22)   | 4.52(4.50)       | 4.84(4.81)       | 13.01(12.90)     | 387   |
| [Eu DDO₂(H₂O)₂] (ClO₄)₃  | 189~190   | 41.12(41.16)   | 4.51(4.49)       | 4.83(4.80)       | 13.09(13.05)     | 382   |

The metal ion was determined by EDTA titration using methenamine as buffer, xylanol orange as an indicator.

IR Spectra

The IR spectra of the complexes are very similar to each other. Table 2. gives the characteristic bands of DDO and the complex.

Table 2. The IR Bands (Cm⁻¹).

| Compounds                  | ν (C=O)  | νₐ(C-O-C) + ν₃(ClO₄⁻) | ν₃(C-O-C) | ν₄(ClO₄⁻) | ν (OH) | ρ(r(H₂O)) |
|----------------------------|----------|-----------------------|-----------|-----------|--------|-----------|
| DDO                       | 1672 vs  | 1159 s                | 948 m     |           |        |           |
| [LaDDO₂(H₂O)₂] (ClO₄)₃   | 1632 vs  | 1065-1109 b r         | 923 m     | 623 s     | 3338, m, br | 602 w    |
| [PrDDO₂(H₂O)₂] (ClO₄)₃   | 1633 vs  | 1053-1108 b r         | 922 m     | 626 s     | 3329, m, br | 598 w    |
| [NdDDO₂(H₂O)₂] (ClO₄)₃   | 1631 vs  | 1049-1107 b r         | 923 m     | 624 s     | 3307, m, br | 605 w    |
| [SmDDO₂(H₂O)₂] (ClO₄)₃   | 1629 vs  | 1071-1104 b r         | 921 m     | 621 s     | 3306, m, br | 604 w    |
| [Eu DDO₂(H₂O)₂] (ClO₄)₃  | 1632 vs  | 1075-1102 b r         | 923 m     | 624 s     | 3334, m, br | 606 w    |

s = strong,  m = middle,  w = weak,  br = broad

The IR spectrum of DDO shows ν(C=O) moved in the direction of low wave number 39~43 cm⁻¹, νₐ(C-O-C) moved in the direction of low wave number 50~57 cm⁻¹, and a strong interference happened between νₐ(C-O-C) and ν₄(ClO₄⁻), in these complex. These indicate that the all acyl and ether oxygen atoms coordinated with Ln³⁺ and formed ring-like structure of coordination.
"\(^1\)H NMR Spectra

The \(^1\)H NMR spectral data of DDO and some of the complexes was showed in Table 3. The data of DDO exhibits multiplet at 7.37 and three singlet at 3.95, 3.72 and 1.10, assigned to (Ph\(-\)), (O=CH\(_2\))\(^-\), (NCH\(_2\))\(^-\) and (-CH\(_3\)) protons, respectively. Upon coordinating all above proton signals shift to lower field, (O=CH\(_2\))\(^-\) shift 0.58 for La complex and 0.60 for Sm complex, (NCH\(_2\))\(^-\) shift 0.12 for La complex and shift 0.15 for Sm complex to lower field. This id due to the inductive effect of Ln(III) ions in the complexes. Above phenomenon indicate that the acyl and ether oxygen atoms are the coordinate atoms. The proton signal of water in these complexes was observed at 2.81 for La complex and 2.76 for Sm complex. This is the trenchancy evidence of some water molecules are in the complex ions. In all the \(^1\)H NMR spectra of the complexes the ratio of the various protons are in good agreement with the elemental analytical results.

| Compound | \(\delta\) (Ph\(-\)) | O \(\delta\) \(\text{C}-\text{CH}_2\) | \(\delta\) (\(\text{CH}_3\)) | \(\delta\) (NCH\(_2\)) | \(\delta\) (H\(_2\)O) |
|----------|-----------------|------------------|-----------------|-----------------|-----------------|
| L        | 7.37(m, 10H)   | 3.95(s, 4H)      | 1.10(t, 6H)    | 3.72(s, 4H)    | -               |
| [LaDDO\(_2\)(H\(_2\)O)\(_2\)](ClO\(_4\))\(_3\) | 7.47(m, 10H)   | 4.43(s, 4H)      | 1.16(s, 6H)    | 3.84(s, 4H)    | 2.81(s, 4H)    |
| [SmDDO\(_2\)(H\(_2\)O)\(_2\)](ClO\(_4\))\(_3\) | 7.52(m, 10H)   | 4.45(s, 4H)      | 1.17(s, 6H)    | 3.87(s, 4H)    | 2.76(s, 4H)    |

s = single, \(m = \text{multiple}\)

Thermal Analysis

All these complexes show similar patterns of decomposition with three weight loss stages. The first loss occurs at 95~113\(^{\circ}\)C corresponding to the loss of two water molecules. The weight losses found in this process compare favorably with the calculated values. Moreover, the relatively high temperatures of dehydration are consistent with the presence of coordinated water molecules, which is inferred from the IR spectral data. The dehydrated complexes are stable up to 290\(^{\circ}\)C and then decompose in the temperature range 270-780\(^{\circ}\)C, producing two exothermic peaks. The initial decomposition temperature of the complex generally increases decreasing ionic radii of the lanthanide ions.

CONCLUSION

The open-chain analogue of crown ethers, N,N'-diethyl-N,N'-diphenyl-3-oxapatanediamide (DDO) can coordinate with lanthanide perchlorates in non-aqueous media to form stable complexes, in which DDO acts as a tridentate ligand, forming the chelates. The molecular formula of the complex should be [Ln(DDO)\(_2\)(H\(_2\)O)\(_2\)](ClO\(_4\))\(_3\) (Ln = La, Pr, Nd, Sm, Eu) and they are stable for heat. Their possible structures are shown in Fig.2.
Fig.2 The possible structure of the complexes

REFERENCES

[1] W. Simon, E. Pretsch, D. Ammann, et al., Recent developments in the field of ion selective electrodes, Pure Appl Chem. 44 (1975) 613-626.
[2] V. E. Weber, F. Vogtle, Kristalline, 1:1-alkalimetall komplexe nichtcyclischer neutral-liganden, Tetrahedron Lett. 29 (1975) 2415-2418.
[3] G. Z. Tan, T. Q. Jiao, Study on open-chain crown in our country, Huaxue Tongbao. 9 (1987) 52-57.61.
[4] H. Narita, T. Yaita, K. Tamura, S. Tachimoris, Solvent extraction of trivalent lanthanoid ions with N,N'-dimethyl-N,N'-diphenyl-3-oxapentanediame, Radiochimica Acta. 81(1998) 223-226.
[5] Y. Sasaki, T. Adachi, G. R. Choppin, Solvent extraction study of actinide elements by N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediame and thenoyltrifluoroacetone, J Alloys Compd. 271-273 (1998) 799-802.
[6] Y. H. Wen, S. Lahir, Z. Qtn, et al., Decontamination of radioactive cesium from natural NaCl by amide-type open-chain crown ethers, J Radio Nucl Chem. 253 (2002) 263-265.
[7] M. Okamoto, K. Takahashi, High-sensitivity detection and postsource decay of 2-aminopyridine- derivatized oligosaccharides with matrix-assisted laser desorption/ ionization mass spectrometry, Analy Chem. 69 (1997) 15-17.
[8] W. Yanr, T. Xiulan, C .Miao, et al., Determination of trace europium based on new fluorimetric system of europium(III) with thenoyltrifluoroacetone and N,N'-diphenyl-3,6-dioxaoctanediamide, Talanta. 46 (1998): 527-532.
[9] C. Alan, P. Ernö, Determination of formal complex formation constants of various Pb²⁺ ionophores in the sensor membrane phase, Anal Chim Acta. 395 (1999) 41-52.
[10] Zh. Zh. Zeng, R. W. Deng, J. G. Wu., Study on the chlorine acid and indomethacin rare earth salts, Huaxue Xuebao. 41 (1983) 909-912.
[11] Y. Hu, L. Zhen, Y. Du et al., Research progress on the application of rare earth elements in oral medicine. Chinese Journal of Practical Stomatoloy, 6 (2013) 756-759.
[12] C. Siemers, F. Brunke, J. Laukart, et al., Rare earth metals in titanium alloys-a systematic study. Goode JR , Moldoveanu G, Rayat MS. Rare Earths 2012 : Proceedings of 51st Conference of Metallurgists. Quebec : The Canadian Institute of Mining , Metallurgy and Petroleum, (2012)281-292.
[13] Y. B. Wang, Y. Shi, T. Q. Jiao, Synthesis and characterization of lanthanide chloride complexes with N,N'-dimethyl-N,N'-diphenyl-3,6-dioxaoctanediame, Journal of Lanzhou University. 38 (2002) 72-75.
[14] B. Wang, Y. Shi, T. Q. Jiao, Synthesis and characterization of lanthanide chloride complexes with \( \text{N,N'}-\text{Diethyl-N,N'}-\text{diphenyl-36-dioxaoctanediame} \), Journal of Lanzhou University (Natural Science Edition), 37 (2001) 126-129.

[15] Y. B. Wang, Y. Shi, Y. H. Wang, et al., Synthesis and characterization of light lanthanide nitrate complexes with \( \text{N,N'}-\text{di(\alpha-aminopyridine)-3,6-dioxaoctaneamid} \), Huaxue Shijie, 1 (2002) 27-30.

[16] T. Q. Jiao, X. M. Gan, M. Y. Tan, et al., Study on amide type open-chain crown ether and rare earth complex, Yingyong Huaxue, 5 (1988) 49-52.

[17] W. J. Geary, The use of conductivity measurements in organic solvents for the characterization of coordination compounds, Coord Chem Rev. 7 (1971):81-122.