

Synthesis of a New Aza-crown Ether Containing Pendant Carboxylate Groups, Its Th⁴⁺ and UO₂²⁺ Complexes and Thermodynamic Properties in Aqueous Solution

JIAN-HONG BI*, FU-XIN XIE†, XIANG-DA ZHAO†, LI-QIN CHEN‡, JI-DE XU** and SHI-SHENG NI†

Department of Chemistry, Anhui Institute of Education, Hefei-230 061, PR China

A novel tetraazamacrocyclic containing pendant carboxylate group L₁H₄ (5, 12-diphenyl-7, 14-dimethyl-1,4,8,11-tetraazamacrocyclotetradecane-N,N',N'',N'''-tetraacetic acid) and its complexes with Th⁴⁺ and UO₂²⁺ have been synthesized and characterized by elemental analyses, IR, ¹H NMR spectra, conductivity measurement, TG-DTA analyses and X-ray powder diffraction. The stability constants of mononuclear complexes of L₁H₄ with the Th⁴⁺ and UO₂²⁺ were determined at 35 ± 0.1, 45 ± 0.1 and 55 ± 0.1°C in 0.5 mol·L⁻¹ KNO₃ solution by means of potentiometric and computer fitting. The ΔH and ΔS of the coordination reactions in the aqueous solution were given.

Key Words: Tetraaza macrocyclic ligand, Thorium(IV), Dioxouranium(VI), Complexes, Stability constants, Enthalpy.

INTRODUCTION

Complexation reactions of metal ions with macrocyclic polyamine ligands have been subjects of numerous investigations in recent years. These complexes have unusual stability, spectroscopic and magnetic properties. Some of the macrocycles are also found to form kinetically inert complexes compared with their noncyclic analogues¹⁻⁴. N-acetates-substituted macrocycles, particularly the tetraazamacrocyclics with four added N-acetates, such as DOTA and TETA (Scheme-1) and some of their derivatives, allow strong complexation of large metal ions that can achieve the coordination number of 8 required for full coordination of the donor atoms of the ligand. These ligands are known to form thermodynamically stable and kinetically inert complexes with a wide range of transitions and lanthanides^{5,6}. These properties make them useful in medical applications, such as in the treatment of metal poisoning intoxications or as contrast-enhancing agent in magnetic resonance or as therapeutical uses^{7,8}. In the search for compounds which may form suitable metal complexes for medical

†Department of Chemistry, Anhui University, Hefei-230 039, PR China.

‡Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada.

**Department of Chemistry, University of California, Berkeley, 94720-1460, USA.

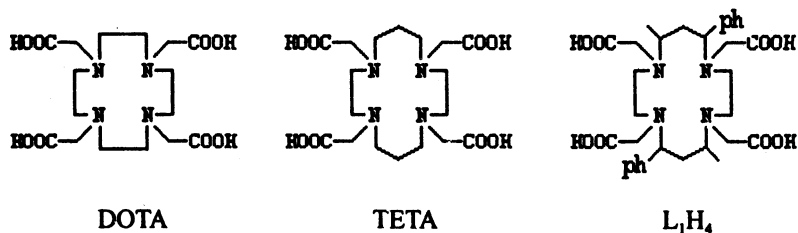
applications, we noticed that the knowledge of these ligands reacting with actinides which may cause health hazards is missing. such as uranium(VI) (UO_2^{2+}) causes kidney damage from chemical interactions, and internally deposited high specific activity uranium isotopes can cause bone cancer⁹.

Trying to fill the gap referred to above, we have prepared a new carboxymethyl derivative of pentadentate macrocycle containing nitrogen and oxygen as donor atoms, L_1H_4 : 5,12-diphenyl-7,14-dimethyl-1,4,8,11-tetraazamacrocyclotetradecane- $\text{N},\text{N}',\text{N}'',\text{N}'''$ -tetraacetic acid (Scheme-1), and its Th^{4+} and UO_2^{2+} complexes. pH potentiometric titrations are employed to estimate temperature-dependent equilibrium constants for reactions of the L_1H_4 with Th^{4+} and UO_2^{2+} in aqueous solution. The thermodynamic parameters of the complexation reactions have been calculated by a linear computer fitting program.

EXPERIMENTAL

All chemicals used were of analytical grade. The solvents were purified by conventional methods. The parent macrocycle meso-meso- $\text{Ph}_2\text{Me}_2[14]\text{janeN}_4$ was prepared by the methods of Hay and Gidney¹⁰ and characterized by elementary analysis and infrared spectroscopy.

Infrared spectra were obtained with a nicolet 170 SX respectively. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer. Conductivity measurements were made with a DDS-11A conductometer. TG-DTA analyses were obtained with a PCT-1 precision thermobalance analyzer. X-ray powder diffraction measurement was made with a XD-3A X-ray diffractometer. Microanalyses were determined by the Centre of Structure and Elemental Analysis, China University of Science and Technology.



Scheme-1

Syntheses of macrocyclic ligand L_1H_4

$\text{L}_1\text{H}_4 \cdot 0.5\text{H}_2\text{O}$ (A): To 55 g (0.4 mol) of bromoacetic acid in 200 mL dry methanol, 0.4 mol of KOH in 300 mL dry methanol was added. Then 25 g (0.066 mol) of meso-meso- $\text{Ph}_2\text{Me}_2[14]\text{janeN}_4$ in 300 mL dry methanol and 43 g (0.4 mol) of powdered anhydrous potassium carbonate were added. The mixture was refluxed with stirring for 24 h, cooled and the white precipitate of KHCO_3 was filtered off. After nearly complete evaporation of the solvent on a rotary evaporator, the residue was dissolved in 300 mL water and the solution was filtered to remove any unreacted cyclic polyamine. The filtrate was acidified to pH 5 with 5 mol L^{-1}

hydrochloric acid. The product $\text{H}_2\text{L}\cdot 0.5\text{H}_2\text{O}$ (A) precipitated as white crystals upon standing. Yield 28 g. The free form of L_1H_4 has not been obtained.

$\text{L}_1\text{H}_4\cdot 2\text{HCl}\cdot 4\text{H}_2\text{O}$ (B): To 15 g of compound A dissolved in 30 mL diluted NaOH solution, 20 mL concentrated hydrochloric acid was added. When the solution cooled slowly, the macrocyclic ligand was precipitated as powder; then white solid (13.7 g) was obtained by recrystallization with water. The product was titrated by KOH and AgNO_3 . $^1\text{H NMR}$ (D_2O): δ 1.15, 1.37 (6H, 2CH_3); 2.30 (4H, $2\text{C}-\text{CH}_2-\text{C}$); 3.33 (12H, $4\text{N}-\text{CH}_2$, $4\text{N}-\text{CH}$); 4.02 (8H, CH_2COOH); 7.46, 7.52 (10H, $2\text{C}_6\text{H}_5$).

Syntheses of Thorium(IV) and Dioxouranium(IV) Complexes

$(\text{Th})_2\text{L}_1\cdot 4\text{NO}_3\cdot 10\text{H}_2\text{O}$: 414 mg (0.75 mmol) of thorium nitrate dissolved in 15 mL methanol was added to a solution of compound B (0.3 mmol in 20 mL methanol), then the mixture was stirred and refluxed for 2 h. The white metal complex crystals were obtained upon standing. These were collected and air dried. Yield 215 mg.

$(\text{UO}_2)_2\text{L}_1\cdot \text{H}_2\text{O}$: To 189 mg (0.25 mmol) of compound B, in 15 mL methanol, 376 mg (0.75 mmol) of uranyl nitrate in 15 mL methanol was added. The mixture was stirred for 1 h, then a light yellow turbid solution formed. The microcrystalline powder precipitated upon standing, collected and air dried at room temperature. Yield 180 mg.

The contents of the thorium and uranium ions in the complexes were determined by EDTA titrations using xylenol orange as an indicator.

Thermogravimetry was done with a PCT-1 precision thermobalance analyzer apparatus at 25 to 550°C (5°C min^{-1}) in air.

Potentiometric Equilibrium Measurements and Computation

The experimental set-up used has been described before¹¹. Typical concentrations of experimental solutions were 1×10^{-4} – 3×10^{-4} mol L^{-1} of ligand with equal molar concentrations of metal ions and then titrated with 0.4 mol L^{-1} KOH at 35 ± 0.1 , 45 ± 0.1 and $55 \pm 0.1^\circ\text{C}$ in 0.5 mol L^{-1} KNO_3 water. All solutions were prepared using double-distilled deionized water.

Calculation of equilibrium constants: Computation of equilibrium constants was made using a program based on the improved TITFIT technique^{11, 12}.

RESULTS AND DISCUSSION

X-ray powder diffraction: The X-ray powder data of the ligand and its Th^{4+} and UO_2^{2+} complexes are listed in Table-1.

Elemental analysis results are given in Table-2. The synthesis of the new complexone-like macrocycle L_1H_4 by akylation of the cyclic tetraamine with bromoacetic acid is straightforward. According to the elemental analysis, L_1H_4 forms 1 : 2 complexes with Th^{4+} and UO_2^{2+} . All ligands and the complexes have crystal water.

TABLE-1
X-RAY POWDER DIFFRACTION DATA OF THE LIGAND AND ITS COMPLEXES

| $L_1H_4 \cdot 2HCl \cdot 4H_2O$ | | | $Th_2L_1 \cdot 4NO_3 \cdot 10H_2O$ | | | $(UO_2)_2L_1 \cdot H_2O$ | | |
|---------------------------------|-------|------------------|------------------------------------|-------|------------------|--------------------------|-------|------------------|
| $2\theta^\circ$ | d, A | I/I ₀ | $2\theta^\circ$ | d, A | I/I ₀ | $2\theta^\circ$ | d, A | I/I ₀ |
| 6.80 | 12.98 | 95.0 | 6.14 | 14.36 | 100.0 | 7.44 | 11.87 | 78.0 |
| 10.14 | 8.72 | 18.2 | 21.42 | 6.74 | 58.4 | 14.50 | 6.24 | 68.2 |
| 13.76 | 6.43 | 23.4 | 30.74 | 4.80 | 48.5 | 17.56 | 5.06 | 100.0 |
| 16.50 | 5.37 | 38.5 | | | | 22.44 | 3.87 | 70.7 |
| 21.38 | 4.15 | 28.2 | | | | | | |
| 24.72 | 3.60 | 100.0 | | | | | | |
| 31.64 | 2.83 | 61.3 | | | | | | |

TABLE-2
ELEMENTAL ANALYSIS OF LIGANDS AND THE METAL-COMPLEXES

| Compound | Analysis: Found (Calcd.) (%) | | | | Yield (%) |
|------------------------------------|------------------------------|----------------|----------------|------------------|-----------|
| | C | H | N | M | |
| $L_1H_4 \cdot 0.5H_2O$ | 61.88 (61.82) | 7.10 (7.30) | 8.90 (9.01) | | 70 |
| $L_1H_4 \cdot 2HCl \cdot 4H_2O$ | 50.48 (50.73) | 7.69 (7.18) | 7.19 (7.39) | | 75 |
| $Th_2L_1 \cdot 4NO_3 \cdot 10H_2O$ | 25.30 (25.60) | 3.87 (4.03) | 7.15 (7.46) | 31.40 (30.91) | 57 |
| $(UO_2)_2L_1 \cdot H_2O$ | 33.02 (32.94) | 4.00 (3.63) | 5.13 (4.80) | 40.25 (40.80) | 62 |

The IR spectral data of ligands and Th^{4+} and UO_2^{2+} complexes and their assignments are given in Table-3. The detailed study of the IR spectra of amino carboxylic acid complexes¹³ has shown that the absorption of the coordinated carboxylate ($COO^- \dots M$) appears in $1640-1625\text{ cm}^{-1}$ region and does not exhibit the band characteristic for the $COOH$ ($1740-1720\text{ cm}^{-1}$) group of the free ligand. For thorium complexes there are no 1385 cm^{-1} absorption peaks, which suggests that the NO_3^- ions exist in coordinated forms, for the uranyl complex exhibits the band characteristic for the UO_2^{2+} (930 cm^{-1}) ion.

TABLE-3
KEY IR SPECTRAL BANDS (cm^{-1}) FOR LIGANDS AND ACTINIDE COMPLEXES

| Compound | $\nu(OH)$ | $\nu(NH^+)$ | $\nu(COOH)$ | $\nu(COO^-)$ | $\nu(C-N)$ | (Coord.) NO_3^- | $\nu(U=O)$ |
|------------------------------------|-----------|-------------|-------------|--------------|------------|-------------------|------------|
| $L_1H_4 \cdot 0.5H_2O$ | 3400 | 2800-2400 | 1720 | 1610 | 1330, 1300 | | |
| $L_1H_4 \cdot 2HCl \cdot 4H_2O$ | 3410 | 2800-2400 | 1740 | 1630 | 1325, 1290 | | |
| $Th_2L_1 \cdot 4NO_3 \cdot 10H_2O$ | 3415 | — | — | 1625 | 1323, 1290 | 748, 817, 1035 | |
| $(UO_2)_2L_1 \cdot H_2O$ | 3400 | — | — | 1640 | 1320, 1286 | | 930 |

Thermogravimetric (TG) analysis: TG data show that for the actinide

complexes, the molar ratio of ligand-actinide is 1 : 2, and the number of hydrated water molecules agree with that of elemental analysis.

Conductivity measurements: Uranyl complex is soluble in water; its molar conductivity value can be neglected, which suggests it to be a nonelectrolyte. Thorium complex is soluble in H₂O, DMF, CH₃NO₂ and DMSO. Its molar conductivity value in water (1×10^{-3} mol L⁻¹) at room temperature is about 520 ·cm²·mol⁻¹, and indicates it to be 1 : 4 electrolytic in nature¹⁴.

Thermodynamic properties

Stability constants: Only mononuclear species was formed (the error square sum $QS \leq 3.1 \times 10^{-3}$). We have checked the possibility of formation of other species, but they are not formed under our experimental conditions. These mononuclear complexes show a marked tendency to protonate and their stability constants are listed in Table-4. As shown in Table-4, the stability constants decrease with an increase of temperature, indicating that the complexation process is more favourable at lower temperatures.

TABLE-4
STABILITY CONSTANTS OF THE COMPLEXES (I = 0.5 mol/L KNO₃)

| Ion | L ₁ H ₄ (35°C) | | L ₁ H ₄ (45°C) | | L ₁ H ₄ (55°C) | |
|-------------------------------|--------------------------------------|-------------------|--------------------------------------|-------------------|--------------------------------------|-------------------|
| | ML ₁ | ML ₁ H | ML ₁ | ML ₁ H | ML ₁ | ML ₁ H |
| Th ⁴⁺ | 12.05 | 5.32 | 10.73 | 4.59 | 9.85 | 3.96 |
| UO ₂ ²⁺ | 9.37 | 3.97 | 8.15 | 2.28 | 7.64 | |

Enthalpies of the coordination reactions: The temperature-dependent data of equilibrium constant in Table-4 can be used to calculate ΔH , ΔS and ΔG for complexation reactions via a van't Hoff analysis with a linear computer fitting program based on the following relationships:

$$(1) \log K = -\Delta H/(2.303RT) + \Delta S/(2.303R) \quad (2) \Delta G = \Delta H - T\Delta S$$

The calculated results are given in Table-5. The negative enthalpy change values and negative Gibbs energy change values for the complexation reactions of L₁H₄ with Th⁴⁺ and UO₂²⁺ indicate that the complexation processes are exothermic and spontaneous in nature.

TABLE-5
CALCULATED ΔH AND ΔS FOR IONIC COMPLEXATION WITH L₁H₄

| Equilibrium | UO ₂ L ₁ = UO ₂ ²⁺ + L ₁ | ThL ₁ = Th ⁴⁺ + L ₁ | ThL ₁ H = Th ⁴⁺ + L ₁ H |
|-------------------------------|---|--|--|
| R ^a | 0.997 | 0.995 | 1.00 |
| - ΔH (kJ/mol) | 168.1 | 213.3 | 131.70 |
| - ΔS (J/K·mol) | 368.2 | 462.8 | 325.70 |
| - $\Delta \bar{G}^b$ (kJ/mol) | 50.98 | 66.12 | 28.08 |

a: Interrelation coefficient of the linear fitting. b: $\Delta \bar{G} = (\Delta G_{308.15 \text{ K}} + \Delta G_{318.15 \text{ K}} + \Delta G_{328.15 \text{ K}})/3$.

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