

Crystal Structure and Thermal Properties of the Lanthanum(III) Complex with Triethylenetetraaminehexaacetic Acid: $K_3[La(TTHA)] \cdot 5H_2O$

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The complex, $K_3[La(TTHA)] \cdot 5H_2O$, was prepared and its crystal structure was analyzed by single crystal X-ray diffraction method. In the complex, the La(III) ion adopts a ten-coordinate geometry with four nitrogen atoms and six carboxyl oxygen atoms from the same TTHA ligand molecule. Its coordination polyhedron can be described as a distorted bicapped square antiprism. Each $[La(TTHA)]^3-$ anion is linked by K^+ cations *via* carboxyl groups of TTHA ligand to form a three dimensional crystal structure. The thermal properties were investigated by TG and DTA techniques in argon atmosphere. The materials resulting from thermal treatment were $La(OH)_3$ and K_2O which were identified by powder X-ray diffraction technique.

Introduction

Lanthanide complexes of polyaminopolycarboxylic acids are being employed extensively in magnetic resonance as MRI contrast reagents and as shift reagents for alkali metal nuclei.¹ Although many ligands such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and triethylenetetraaminehexaacetic acid (TTHA), have been used for these purposes, the most useful of these ligands is TTHA.² On the other hand, among the three diamagnetic nuclei, lanthanum ($^{139}La^{3+}$), lutetium ($^{175}Lu^{3+}$) and ytterbium ($^{173}Yb^{2+}$) in lanthanides, lanthanum appears to be only one of the NMR plausible nuclei for the study of the coordination properties of cations. In practice, lanthanum(III) cations already have been proposed as model for Ca^{2+} binding sites to study coordination properties in proteins³ and $^{139}La^{3+}$ NMR has been used for the analytical tool of relevant nucleus.⁴

It has been previously known that EDTA and DTPA have 6 coordination numbers (2 nitrogens and 4 carboxylates) and 7 coordination numbers (3 nitrogens and 4 carboxylates) with alkaline earth and diamagnetic lanthanide cations (La^{3+} , Lu^{3+} and Y^{3+}), respectively.⁵ However, in the case of the TTHA, the coordination number of the lanthanide-TTHA complex in solution state is still controversial. More specifically, there are two proposals: one with eight coordination number (4 nitrogens and 4 carboxylates) and other involving six coordination number (2 nitrogens and 4 carboxylates, 4 nitrogens and 2 carboxylates).^{6,7} The fact that TTHA ligand can not donate all 10 possible donor atoms is well supported by the ligand-induced ^{139}La NMR chemical shift.⁶

Since the ligand has been proposed for a variety of analytical uses, stability constants, thermodynamic and structural properties of lanthanide complexes with TTHA in aqueous solution have been widely studied.^{5,7-11} On the other hand, there are only a few reports concerning the solid state X-ray structural results for the complexes of this TTHA ligand with lanthanide ion.¹²⁻¹⁵ Although the La-TTHA crystal

structure was reported recently by Wang *et al.*,¹³ the features of crystal structure, and the coordination of potassium ion and water molecules is significantly different. Therefore, we here report the solid state X-ray crystal structure, $K_3[La(TTHA)] \cdot 5H_2O$, and molecular structure, and the thermal properties of the lanthanum complex.

Experimental Section

Preparation and analysis of $K_3[La(TTHA)] \cdot 5H_2O$. The complex was prepared by adding 6 equiv. KOH slowly to a 50 mL of an aqueous solution containing 1 equiv. TTHA and $LaCl_3$. The resulting solution was slowly evaporated by heating. A white precipitate of KCl was formed, and filtrated. The filtrate was concentrated and evaporated slowly. The colorless block crystals were formed at the bottom of the pyrex beaker.

The content of C, H, and N was determined by a CE EA-1110 elemental analyzer. The content of K and La was determined by Perkin-Elmer 2380 atomic absorption spectrometer and Thermo-Jarrell Ash AtomScan-25 inductively coupled plasma emission spectrometer, respectively. The composition of the complex crystal was deduced from the elemental analyses: the formula of $K_3[La(TTHA)] \cdot 5H_2O$ is consistent with the results of single crystal X-ray diffraction analysis. *Anal. Found.*: C, 25.56; H, 4.06; N, 6.67; K, 14.20; La, 17.01%. *Calc. for $C_{18}H_{34}N_4O_{11} \cdot K_3La$* : C, 25.90; H, 4.11; N, 6.71; K, 14.05; La, 16.64%.

Infrared spectra of the lanthanum(III) complex and free ligand were recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr disk methods at the room temperature. The thermal properties were investigated with a TA Instruments SDP-2960 thermal analyzer under dynamic conditions. Al_2O_3 was used as the standard substance, samples were placed inside an alumina crucibles. Thermal decomposition was carried out at a rate of 10 °C/min, from room temperature to 1000 °C under an argon atmosphere. A powder X-ray diffraction pattern of the material obtained

Table 1. Crystallographic and experimental data for $K_3[La(TTHA)] \cdot 5H_2O$

Empirical formula	$C_{18}H_{31}N_4O_{17}K_3La$
Formula weight	834.70
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.7139(11)
b (Å)	16.156(3)
c (Å)	21.076(3)
α (°)	107.766(11)
β (°)	92.013(11)
γ (°)	107.319(13)
V (Å ³)	2977.9(7)
Z	4
D_x, D_m^a (g/cm ³)	1.862, 1.86(1)
$F(000)$	1680
μ (Mo-K α) (mm ⁻¹)	1.935
Crystal size (mm)	0.3×0.4×0.3
Temperature (K)	294(2)
λ (Å) (Mo-K α)	0.71073
θ range for data (°)	1.99–27.50
Limiting indices	$-12 < h < 1, -19 < k < 19, -27 < l < 27$
Reflections collected	15853
Independent reflections	13456 [$R_{int} = 0.0461$]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.4974, 0.4429
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13454 / 0 / 775
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0301, wR_2 = 0.0774$
R indices (all data)	$R_1 = 0.0374, wR_2 = 0.0821$
Largest diff. peak and hole (e/Å ³)	0.751, -0.790

^aThe experimental density of the crystal was measured by the flotation method in bromoform-mesitylene.

from thermal treatment of $K_3[La(TTHA)] \cdot 5H_2O$. was recorded on a Rigaku D/MAX-III B X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) in the 2θ range 3–60°.

Single crystal X-ray diffractometry. The crystallographic and experimental data are summarized in Table 1. A colorless single crystal of the title compound was coated with epoxy resin in order to prevent spontaneous liberation of water molecules from the specimen under ambient conditions. The intensity data were collected at room temperature on a Siemens P4 four-circle X-ray diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Accurate unit cell dimensions were refined using 48 reflections with 2θ ranges 8.04–25.04°. Three standard reflections were measured every 97 reflections; no remarkable decays were observed. The reflections used with the intensities $|I - 2\sigma|$ were Lorentz and polarization corrected; a semi-empirical absorption correction based on the psi-scans was applied. A total of 15853 reflections was collected in the 2θ range 3.5–55.0° using 2θ - θ scan mode.¹⁶

All calculations in the structural solution and refinement was performed using the Siemens SHELXTL crystallo-

graphic software package¹⁷ on a Silicon Graphics system. Space groups were assigned based on the systematic absences and intensity statistics, and were confirmed by successful refinements. The structure was solved by the direct method¹⁸ and refined by successive full-matrix least-squares method followed by difference Fourier map. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features.

Results and Discussion

The observed systematic absences were consistent with the space group $P\bar{1}$ and $P\bar{1}$: the space group $P\bar{1}$ was finally adopted because it gave the better convergence results. The selected bond distances and bond angles are listed in Table 2. Tables of the structure factors, refined atomic coordinates, anisotropic thermal parameters, and calculated positions of

Table 2. Selected bond distances (Å) and angles (°) for $K_3[La(TTHA)] \cdot 5H_2O$

La(1)–O(1)	2.586(2)	La(1)–O(3)	2.575(2)
La(1)–O(5)	2.488(2)	La(1)–O(7)	2.523(3)
La(1)–O(9)	2.517(2)	La(1)–O(11)	2.576(3)
La(1)–N(1)	2.794(2)	La(1)–N(2)	2.804(3)
La(1)–N(3)	2.798(3)	La(1)–N(4)	2.913(3)
La(2)–O(21)	2.603(2)	La(2)–O(23)	2.550(2)
La(2)–O(25)	2.516(2)	La(2)–O(27)	2.499(2)
La(2)–O(29)	2.568(2)	La(2)–O(31)	2.545(2)
La(2)–N(5)	2.789(2)	La(2)–N(6)	2.804(3)
La(2)–N(7)	2.792(3)	La(2)–N(8)	2.885(3)
K(1)–O(1)* ¹	2.905(2)	K(1)–O(2)* ¹	2.912(3)
K(1)–O(3)	3.244(3)	K(1)–O(4)* ²	2.937(3)
K(1)–O(9)	2.667(2)	K(1)–O(11)* ¹	3.150(3)
K(1)–O(12)* ¹	2.689(3)	K(1)–O(3w)	3.370(4)
K(2)–O(3)	2.707(2)	K(2)–O(4)* ²	2.739(3)
K(2)–O(5)	2.841(3)	K(2)–O(9)	2.955(2)
K(2)–O(10)	2.871(3)	K(2)–O(12)* ³	2.541(3)
K(2)–O(2w)	2.706(6)	K(3)–O(2)* ¹	2.717(3)
K(3)–O(4)* ²	2.815(3)	K(3)–O(10)	2.747(3)
K(3)–O(32)	2.728(2)	K(3)–O(3w)	2.915(4)
K(3)–O(7w)	2.879(4)	K(4)–O(10)	2.702(2)
K(4)–O(22)* ¹	2.815(3)	K(4)–O(24)* ⁵	2.856(2)
K(4)–O(32)	2.808(3)	K(4)–O(1w)	2.844(3)
K(4)–O(2w)	3.165(7)	K(4)–O(6w)	2.892(3)
K(5)–O(23)	2.729(2)	K(5)–O(24)* ⁵	2.706(2)
K(5)–O(25)	2.883(2)	K(5)–O(30)* ³	2.552(3)
K(5)–O(31)	2.866(2)	K(5)–O(32)	2.900(3)
K(5)–O(4w)	3.301(5)	K(5)–O(5w)	2.890(4)
K(6)–O(21)	2.889(2)	K(6)–O(22)* ¹	2.866(3)
K(6)–O(23)	3.297(3)	K(6)–O(24)* ⁵	2.803(2)
K(6)–O(29)* ¹	3.176(3)	K(6)–O(30)* ¹	2.677(3)
K(6)–O(31)	2.697(2)	K(6)–O(1w)	3.250(3)
La(1)···K(1)	4.141(1)	La(1)···K(2)	4.144(1)

Table 2. Continued

La(2)···K(5)	4.129(1)	La(2)···K(6)	4.062(1)
K(1)···K(3)	3.661(1)	K(2)···K(3)	4.016(1)
K(3)···K(4)	4.288(1)	K(4)···K(5)	4.065(1)
K(4)···K(6)	3.629(1)	K(5)···K(6)	3.954(1)
O(1)-La(1)-O(3)	74.32(8)	O(1)-La(1)-O(5)	140.91(8)
O(1)-La(1)-O(7)	90.52(8)	O(1)-La(1)-O(9)	68.23(8)
O(1)-La(1)-O(11)	79.96(7)	O(3)-La(1)-O(5)	71.39(7)
O(3)-La(1)-O(7)	130.52(8)	O(3)-La(1)-O(9)	138.33(9)
O(3)-La(1)-O(11)	70.34(7)	O(5)-La(1)-O(7)	126.26(8)
O(5)-La(1)-O(9)	132.81(8)	O(5)-La(1)-O(11)	71.34(7)
O(7)-La(1)-O(9)	68.36(10)	O(7)-La(1)-O(11)	153.85(8)
O(9)-La(1)-O(11)	85.50(9)	O(1)-La(1)-N(1)	60.04(7)
O(3)-La(1)-N(1)	62.39(7)	O(5)-La(1)-N(1)	116.53(7)
O(7)-La(1)-N(1)	69.18(8)	O(9)-La(1)-N(1)	110.56(8)
O(11)-La(1)-N(1)	123.86(7)	O(1)-La(1)-N(2)	124.70(7)
O(3)-La(1)-N(2)	75.09(8)	O(5)-La(1)-N(2)	62.67(8)
O(7)-La(1)-N(2)	76.24(8)	O(9)-La(1)-N(2)	142.70(10)
O(11)-La(1)-N(2)	129.03(8)	O(1)-La(1)-N(3)	148.48(8)
O(3)-La(1)-N(3)	134.96(8)	O(5)-La(1)-N(3)	70.27(8)
O(7)-La(1)-N(3)	62.26(8)	O(9)-La(1)-N(3)	86.05(9)
O(11)-La(1)-N(3)	117.12(8)	O(1)-La(1)-N(4)	112.80(7)
O(3)-La(1)-N(4)	125.07(7)	O(5)-La(1)-N(4)	74.05(7)
O(7)-La(1)-N(4)	104.32(8)	O(9)-La(1)-N(4)	58.83(8)
O(11)-La(1)-N(4)	58.72(7)	N(1)-La(1)-N(2)	65.12(7)
N(1)-La(1)-N(3)	117.37(8)	N(1)-La(1)-N(4)	169.38(7)
N(2)-La(1)-N(3)	66.86(8)	N(2)-La(1)-N(4)	122.49(7)
N(3)-La(1)-N(4)	63.94(8)	O(21)-La(2)-O(23)	75.40(7)
O(21)-La(2)-O(25)	142.99(7)	O(21)-La(2)-O(27)	89.21(7)
O(21)-La(2)-O(29)	67.81(8)	O(21)-La(2)-O(31)	82.31(7)
O(23)-La(2)-O(25)	72.19(7)	O(23)-La(2)-O(27)	128.39(7)
O(23)-La(2)-O(29)	139.99(9)	O(23)-La(2)-O(31)	70.81(7)
O(25)-La(2)-O(27)	125.13(7)	O(25)-La(2)-O(29)	133.79(8)
O(25)-La(2)-O(31)	70.60(7)	O(27)-La(2)-O(29)	67.42(9)
O(27)-La(2)-O(31)	156.21(8)	O(29)-La(2)-O(31)	88.81(8)
O(21)-La(2)-N(5)	59.89(7)	O(23)-La(2)-N(5)	62.53(7)
O(25)-La(2)-N(5)	117.00(7)	O(27)-La(2)-N(5)	67.10(7)
O(29)-La(2)-N(5)	108.75(7)	O(31)-La(2)-N(5)	125.11(7)
O(21)-La(2)-N(6)	124.26(7)	O(23)-La(2)-N(6)	74.55(8)
O(25)-La(2)-N(6)	62.59(7)	O(27)-La(2)-N(6)	74.78(8)
O(29)-La(2)-N(6)	140.36(9)	O(31)-La(2)-N(6)	128.08(7)
O(21)-La(2)-N(7)	146.28(7)	O(23)-La(2)-N(7)	135.75(8)
O(25)-La(2)-N(7)	70.43(7)	O(27)-La(2)-N(7)	62.12(8)
O(29)-La(2)-N(7)	84.00(9)	O(31)-La(2)-N(7)	116.43(7)
O(21)-La(2)-N(8)	112.08(7)	O(23)-La(2)-N(8)	126.47(7)
O(25)-La(2)-N(8)	75.08(7)	O(27)-La(2)-N(8)	105.05(8)
O(29)-La(2)-N(8)	59.03(8)	O(31)-La(2)-N(8)	58.80(7)
N(5)-La(2)-N(6)	64.72(7)	N(5)-La(2)-N(7)	116.86(8)
N(5)-La(2)-N(8)	167.77(7)	N(6)-La(2)-N(7)	67.75(8)
N(6)-La(2)-N(8)	123.58(8)	N(7)-La(2)-N(8)	63.85(8)

Symmetry transformations used to generate equivalent atoms: [†]1; -x-1, -y+1, -z+1; [‡]2; -x+2, -y+1, -z+1; [§]3; x+1, y, z; [¶]4; x-1, y+1, z; ^{**}5; -x-1, -y+1, -z.

hydrogen atoms have been deposited as the supplementary material.

The coordination geometry of the title complex anion

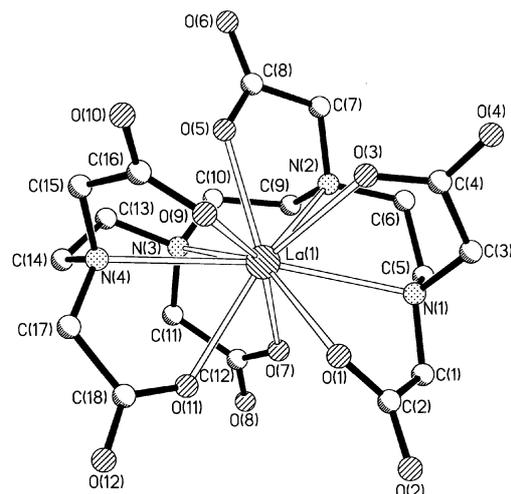


Figure 1. The lanthanum coordination environment of $[La(TTHA)]^{3-}$ complex anion with atomic numbering. The hydrogen atoms are omitted for the sake of clarity.

$[La(TTHA)]^{3-}$ is shown in Figure 1. As shown in Figure 1, La^{3+} metal ion is encapsulated by one TTHA ligand molecule, and the structural coordination feature is ten-coordinated by six oxygen atoms from the six carboxyl groups and four nitrogen atoms of the TTHA molecule. Its coordination polyhedron feature can be described as a distorted bicapped square antiprism arrangement. As listed in Table 2, the La-O bond distances range from 2.488(2) to 2.603(2) Å, and the La-N bond distances range from 2.789(2) to 2.913(3) Å; these results indicate the La-O bond strength is more stable than the La-N bond strength because the La-N bond distances are considerably greater than that of the La-O bond. Bond distances and bond angles in the TTHA ligand are the same within the experimental errors as the previous reported results.^{19,20}

The asymmetric unit of $K_3[La(TTHA)] \cdot 5H_2O$ is shown in Figure 2. As shown in Figure 2, each $[La(TTHA)]^{3-}$ anion is linked by K^+ cations *via* carboxyl groups of TTHA ligand to form a three dimensional networks. As listed in Table 2, K-O (oxygen atoms of TTHA ligand) bond distances range from 2.541(3) to 3.176(3) Å, K-O (bridged oxygen atoms from water molecules) bond distances range from 2.706(6) to 3.370(4) Å, K-O (coordinated oxygen atoms from water molecules) bond distances range from 2.879(4) to 3.301(5) Å. La···K distances range from 4.062(1) to 4.144(1) Å,

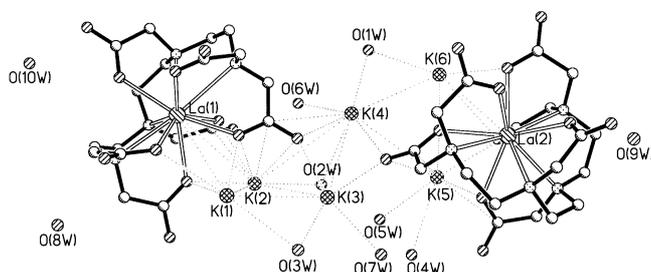


Figure 2. The asymmetric unit of $K_3[La(TTHA)] \cdot 5H_2O$. The atomic numbering of TTHA ligand are omitted for the sake of clarity.

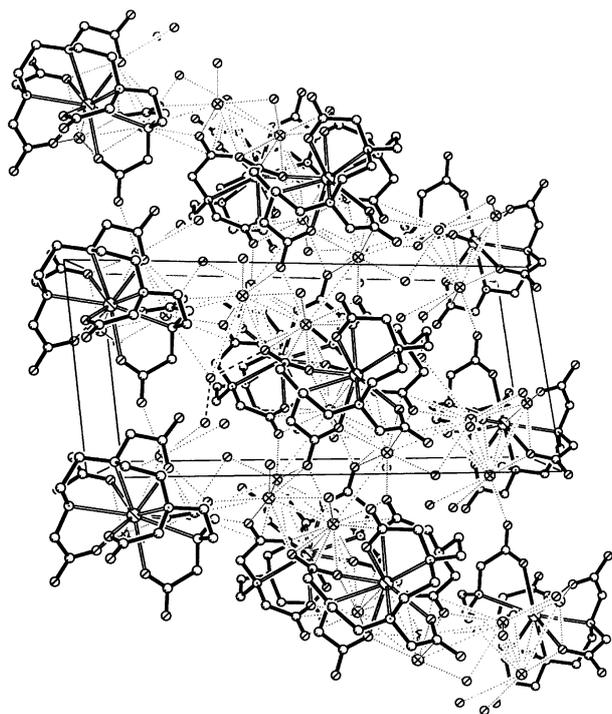


Figure 3. A perspective view of the unit cell of $K_3[La(TTTHA)] \cdot 5H_2O$ along the b -axis.

$K \cdots K$ distances range from 3.629(1) to 4.288(1) Å. On the other hand, there are three kinds of potassium ions in the crystal. K(1), K(2) and K(6) ions are coordinated by oxygen atoms from TTTHA molecules and bridged by oxygen atom from water molecule. K(3) and K(4) ions are coordinated by oxygen atoms from TTTHA molecules, and are not only bridged by oxygen atom from water molecule but also coordinated by oxygen atom from water molecule. K(5) ion is coordinated by oxygen atoms from TTTHA molecules and water molecules. In addition, three kinds of crystallographically independent water molecules are present in the crystal; O(1w), O(2w) and O(3w) water molecules are bridged to K^+ cations, O(4w), O(5w), O(6w) and O(7w) water molecules are coordinated to K^+ cations, O(8w), O(9w) and O(10w) water molecules are un-bridged and un-coordinated free water molecule.

The crystal structure of the title compound can be described as having a three-dimensional infinite network as shown in Figure 3. By the packing of the discrete complex molecule linked by K^+ cations *via* carboxyl groups of TTTHA ligand, the crystal structure is constructed a three dimensional networks and furthermore stabilize by the crystal packing through hydrogen bonds. Although the coordination polyhedron of lanthanum metal ion reported by Wang *et al.*¹³ for $K[KLa(HTTTHA)(H_2O)] \cdot 8H_2O$ is essentially the same as that reported for $K_3[La(TTTHA)] \cdot 5H_2O$ in this work, the coordination structures and behaviors of potassium cations and water molecules are significantly different. The most significant difference is that the lanthanum ion does not have any direct contact bond with water molecules which generally has the important role in imaging experiment. In addition,

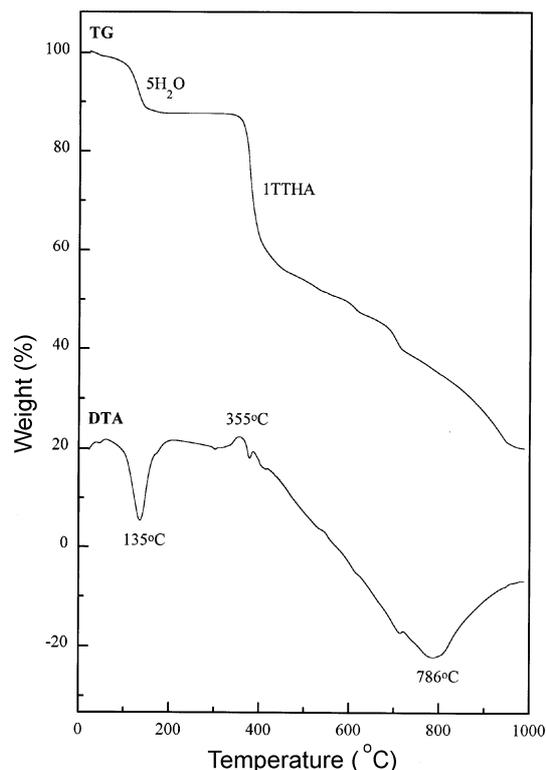


Figure 4. Thermogravimetric analyses of $K_3[La(TTTHA)] \cdot 5H_2O$.

tion, the detailed crystal structure and thermal properties of the compound were not reported.

IR spectra of the studied lanthanum(III) complex and free TTTHA ligand were obtained. The assignment of the relevant observed absorption bands was made on the basis of the reported data.²¹ For the sake of comparison the corresponding absorption bands observed in the IR spectra of the lanthanum complex and free ligand are summarized as follows: the antisymmetric stretching frequency (ν_{as}) of carboxyl group in the complex is shifted 47 cm^{-1} to lower frequency from 1642 cm^{-1} and the symmetric stretching frequency (ν_s) of carboxyl group in the complex is shifted 10 cm^{-1} to higher frequency from 1398 cm^{-1} . These results provide further support to X-ray analysis that the carboxyl groups of the TTTHA ligand have been coordinated with the lanthanum metal ion. A broad absorption band for hydroxyl group appeared at 3400 cm^{-1} in the complex indicates the presence of water molecules.

The thermal decomposition of the lanthanum complex, $K_3[La(TTTHA)] \cdot 5H_2O$, is represented in Figure 4. In the first stage of the thermal decomposition are liberated of water molecules which manifests itself on the TG curve as a weight loss of 10.90 % (equivalent to $5H_2O$) and DTA curve as an endothermic process at 135 °C. This result is in accordance with the X-ray crystal structure analysis of this compound to be $K_3[La(TTTHA)] \cdot 5H_2O$. After losing water molecules the total endothermic decomposition of the lanthanum complex was observed at range from 357-987 °C, and the various compounds derived from TTTHA ligand were slowly released. The final products were obtained at 1000 °C

after thermal analysis, and characterized by powder X-ray diffraction technique. The final products were mixture of $La(OH)_3$ and K_2O .

The structural and spectroscopic studies in solid and solution state for the lanthanide complexes of polyaminopolycarboxylic acids such as EDTA, DTPA and TTHA, are in progress presently.

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