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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF $Me_2NC_6H_4CH{=}CHC_5H_4N(C_2H_5)^+[La(TTA)_4]^-$(TTA = α-THENOYLTRIFLUOROACETONATO)

KE-ZHI WANG, CHUN-HUI HUANG* and GUANG-XIAN XU

State Key Laboratory of Rare Earth Materials Chemistry and Applications,
Peking University, Beijing 100871, P.R. China

and

RU-JI WANG

Analysis Center, Tsinghua University, Beijing 100084, P.R. China

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Abstract—The complex (*E*)-*N*-ethyl-4-(2-(4′-dimethylaminophenyl)ethenyl)pyridinium tetrakis(α-thenoyltrifluoroacetonato)lanthanum(III) was synthesized, and its crystal structure was determined by single-crystal X-ray crystallography and refined to the final R of 0.046 and R_w of 0.052. IR, electronic absorption spectroscopy (UV–vis) and thermogravimetric and differential thermal analysis (TG–DTA) for the complex are also reported.

Dimethylaminostilbazolium chromophores (hemicyanines) possess large second-order molecular hyperpolarizability. Studies on second-harmonic generation (SHG) from the powders[1,2] and Langmuir–Blodgett (LB) films[3–5] of the hemicyanines have attracted much attention due to their potential applications in various areas of optoelectronics.[6] Second-order non-linear optical properties of the materials are sensitive to the symmetry of the structure; in this regard, it is imperative that the structure–property relationship be studied.[7] Marder *et al.*[2] reported that the variation of counterion in organic salts is a simple and highly successful approach to creating materials with very large χ; this methodology was also supported by the crystal structure of $(CH_3)_2NC_6H_4{-}CH{=}CH{-}C_5H_4N(CH_3)^+p{-}CH_3C_6H_4SO_3^-$.[1] Using a lanthanide complex as the counterion of hemicyanine and spacer of LB films, we greatly improved the LB film-forming and second-order non-linear optical properties.[5] In order to best understand this phenomenon, the title complex was synthesized and was structurally studied by single-crystal X-ray diffractometry.

Lanthanide complexes with α-thenoyltrifluoroacetone (HTTA) had been widely studied in order to search for luminescent materials and NMR shift reagents.[8] The crystal structures of these complexes are mainly concerned with $Ln(TTA)_3 \cdot B_n$ ($n = 1$ or 2, B stands for organic neutral ligands containing P=O and N—O groups);[9,10] the structures of type $Q^+[Ln(TTA)_4]^-$ are limited.[11–13] To our knowledge, the crystal structures of hemicyanines containing metal complexes as counterions have not so far been reported.

EXPERIMENTAL

Synthesis of 4-*methyl*-N-*ethylpyridinium bromide* (A)

An ethanolic solution of equal molarities of 4-methylpyridine and ethyl bromide was refluxed for 24 h. Most of the solvent was evaporated off in a water bath under reduced pressure and was then placed in a refrigerator. Coloured supernatant liquid was decanted off. This operation was

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* Author to whom correspondence should be addressed.

repeated several times until the supernatant had scarcely visible colour. The product was dried *in vacuo* over H_2SO_4 for several days and can be used for the following synthetic step without further purification. The product is very hygroscopic and would become liquid very quickly if left in air.

Synthesis of (E)-N-*ethyl*-4-(2-(4′-*dimethylaminophenyl*)*ethylene*)*pyridinium bromide* (**B**)

A mixture of **A** (4 mmol) and 4-dimethylaminobenzaldehyde (4 mmol) in dried ethanol was treated with piperidine (0.4 cm^3) and was refluxed for 4 h. The resulting suspension was cooled. The precipitate was filtered off and recrystallized from hot ethanol. Found: C, 60.8; H, 6.3; N, 8.5; Br, 23.8. Calc. for $C_{17}H_{21}N_2Br$: C, 61.3; H, 6.3; N, 8.4; Br, 24.0%.

Synthesis of (E)-N-*ethyl*-4-(2-(4′-*dimethylaminophenyl*)*ethylene*)*pyridinium tetrakis*(α-*thenoyltrifluoroacetonato*)*lanthanum* (III)

To a mixture of 1 mmol of **B** and 4 mmol of HTTA neutralized with 4 mmol aqueous ethanol–NaOH solution was added dropwise 1 mmol of aqueous $La(NO_3)_3$ under constant stirring. The resulting precipitate was filtered off. A nearly saturated solution of the precipitate in 95% ethanol was allowed to evaporate slowly, and after 2 weeks red single crystals were obtained. Found: C, 46.3; H, 2.9; N, 2.2, La, 10.9. Calc. for $C_{49}H_{37}N_2F_{12}O_8S_4La$: C, 46.1; H, 2.9; N, 2.2; La, 10.9%.

Spectroscopic measurements

The IR spectra in the 400–4000 cm^{-1} region (as KBr pellets) were recorded on a 7199 B FT-IR system. UV–vis spectra were obtained with a Shimadzu 240 spectrophotometer. Thermogravimetric and differential thermal analysis was carried out on an LCT-1 system.

X-ray data collection, structural solution and refinement

A crystal of $0.1 \times 0.15 \times 0.3$ mm^3 in size was mounted on an Enraf–Nonius CAD4 diffractometer. The equipment operated in the ω–2θ scan mode and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) was used. 3143 Independent reflections were collected at room temperature (23 ± 1°C) in the range of $2° \leqslant \theta \leqslant 23°$, of which 1840 observed reflections [$I \geqslant 3\sigma(I)$] were used for structural refinement. All intensities were corrected for Lorentz and polarization effects and an absorption correction was applied. The crystal was solved by the heavy-atom method. The central lanthanum atom was deduced from the Patterson maps, while all the other non-hydrogen atoms were located by means of successive Fourier syntheses. The coordinates of all non-hydrogen atoms and anisotropic thermal parameters were refined by full-matrix least-squares and gave final values of $R = 0.046$ and $R_w = 0.052$. All the calculations were carried out on a PDP 11/44 computer using the SDP-PLUS package.

The crystal data and additional details are as follows: the crystal belongs to monoclinic space group $C2/c$, $a = 2.7356(6)$, $b = 1.0414(2)$, $c = 2.4032(5)$ nm, $\beta = 129.95(2)°$, $V = 5.248(2)$ nm^3, $M_r = 1276.95$, $Z = 4$, $D_{calc} = 1.62$ g cm^{-3}, $\mu = 10.7$ cm^{-1}, $F(000) = 2552$.

RESULTS AND DISCUSSION

Description of the structure

Bond distances (nm) and angles (°) for the complex are given in Tables 1 and 2, respectively. Figure 1 shows the structure of the complex together with the atom labelling scheme. The lanthanum atom is coordinated by the eight oxygens from four bidentate deprotonated TTA^- ligands and is located on the two-fold axis of the unit cell. The eight coordinated oxygen atoms take a square antiprism con-

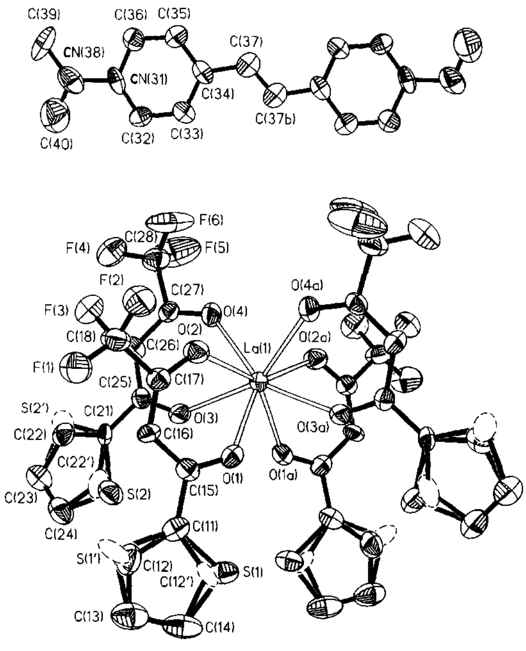

Fig. 1. The labelling scheme of the complex. Symmetry transformations: a = $(-x, y, 1.5-z)$; b = $(-x, -y, 1-z)$.

Table 1. Bond distances (nm) for the title complex

La coordination polyhedron					
La(1)—O(1)	0.2495(3)	La(1)—O(2)	0.2507(3)	La(1)—O(3)	0.2463(3)
La(1)—O(4)	0.2472(3)				
α-Thenoyltrifluoroacetone ligand					
C(11)—C(15)	0.149(1)	O(1)—C(15)	0.121(1)	C(16)—C(17)	0.136(2)
O(2)—C(17)	0.127(1)	C(17)—C(18)	0.154(1)	C(25)—C(26)	0.144(2)
O(3)—C(25)	0.127(2)	C(26)—C(27)	0.137(2)	O(4)—C(27)	0.1244(5)
C(27)—C(28)	0.151(2)				
(*E*)-*N*-Ethyl-4-(2-(4-dimethylaminophenyl)ethyl)pyridinium					
CN(31)—C(32)	0.140(2)	C(34)—C(37)	0.147(2)	CN(31)—C(36)	0.142(3)
C(35)—C(36)	0.138(2)	CN(31)—CN(38)	0.150(2)	C(37)—C(37b)	0.129(3)
C(32)—C(33)	0.141(2)	CN(38)—C(39)	0.139(3)	C(33)—C(34)	0.141(2)
CN(38)—C(40)	0.124(4)	C(34)—C(35)	0.141(2)		

Table 2. Bond angles (°) for the title complex with standard deviations in parentheses

La coordination polyhedron					
O(1)—La(1)—O(1a)	77.3(3)	O(2)—La(1)—O(3)	81.7(3)	O(1)—La(1)—O(2)	67.9(2)
O(2)—La(1)—O(3b)	109.3(3)	O(1)—La(1)—O(2a)	142.0(2)	O(2)—La(1)—O(4)	80.6(3)
O(1)—La(1)—O(3)	73.8(3)	O(2)—La(1)—O(4a)	77.5(2)	O(1)—La(1)—O(3a)	74.1(2)
O(3)—La(1)—O(3a)	138.5(3)	O(1)—La(1)—O(4)	133.7(2)	O(3)—La(1)—O(4)	68.6(3)
O(1)—La(1)—O(4a)	115.6(3)	O(3)—La(1)—O(4a)	150.9(2)	O(2)—La(1)—O(2a)	149.4(3)
O(4)—La(1)—O(4a)	88.0(4)				
α-Thenoyltrifluoracetone ligand					
La(1)—O(1)—C(15)	132.3(8)	C(15)—C(16)—C(17)	120.6(8)		
La(1)—O(2)—C(17)	129.7(7)	O(2)—C(17)—C(16)	131.5(9)		
O(1)—C(15)—C(16)	125.4(9)	La(1)—O(3)—C(25)	139.9(6)		
O(3)—C(25)—C(26)	123.3(10)	La(1)—O(4)—C(27)	134.8(6)		
C(21)—C(25)—C(26)	119.7(5)	C(25)—C(26)—C(27)	121.2(12)		
O(4)—C(27)—C(26)	130.6(11)				
(*E*)-*N*-Ethyl-4-(2-(4-dimethylaminophenyl)pyridinium					
C(32)—CN(31)—C(36)	120.8(11)	C(35)—C(34)—C(37)	117.8(15)		
C(32)—CN(31)—CN(38)	126.2(15)	C(34)—C(35)—C(36)	121.9(4)		
C(36)—CN(31)—CN(38)	112.9(14)	CN(31)—C(36)—C(35)	118.8(15)		
CN(31)—C(32)—C(33)	118.9(16)	C(34)—C(37)—C(37b)	123.4(21)		
C(32)—C(33)—C(34)	121.7(15)	CN(31)—CN(38)—C(39)	126.5(19)		
C(33)—C(34)—C(35)	117.6(11)	CN(31)—CN(38)—C(40)	111.0(18)		
C(33)—C(34)—C(37)	117.8(15)	C(39)—CN(38)—C(40)	122.3(18)		

Symmetry transformations: a = $(-x, y, 1.5-z)$; b = $(-x, -y, 1-z)$

figuration in contrast to the dodecahedral structure reported for the $Pr(TTA)_4$ ion in the ammonium salt[12] and $Ce(TTA)_4$ in the isoquinolium salt.[13] One plane consists of O(1), O(2), O(3a) and O(4a), the other of O(1a), O(2a), O(3) and O(4). Both of them are of good planarity, the dihedral angle between the two planes is 5.2°. The La—O bond distances range from 0.2472 to 0.2507 nm, and there is significant deviation from the average La—O bond length of 0.2484(3) nm, slightly smaller than the sum of ionic radii 0.251 nm (eight-coordinated La^{3+} 0.116 nm[14] and O^{2-} 0.135 nm).

In the β-diketone chelate rings, the mean C—C and C—O distances, 0.145 and 0.126 nm, and the mean C—C—C angle, 117.1°, are compatible with the values reported for the delocalized systems of β-diketonates.[15,16] Significant differences occur between the C—C—O angle of 131° adjacent to the trifluoromethyl group and that (120.9°) at the other end of the ligand; namely trifluoromethyl results in the increase in the β-diketone chelate ring angle.[12] It should be pointed out that each thienyl ring in the ligand TTA^- is disordered due to the free rotation of the C—C σ-single bond.

The bulky complex anion, $La(TTA)_4$, formed by the coordination of La^{III} with TTA^-, is balanced in charge by the hemicyanine cation with a *trans* configuration. The hemicyanine cation is not centrosymmetric, but the Fourier syntheses gave a centrosymmetric model with the centre located at the crystallographic inverse centre (0, 0, 0.5). This is due to the fact that X-ray diffraction data are insensitive to the difference between nitrogen and carbon atoms, and the hemicyanine cation and N-ethyl groups are orientationally disordered. This results in a statistically centrosymmetric model.

UV–vis spectra

In the visible spectrum of the lanthanum complex in $CHCl_3$, there is a peak at 492 nm due to transition on the hemicyanine chromophore. In the UV region, the absorption of the hemicyanine cation is very weak relative to the complex anion. Therefore, in the lanthanum complex there are two peaks which are mainly contributed by the complex anion: one at 272 nm, due to $\pi \rightarrow \pi^*$ transition of the thienyl group, basically remains unchanged compared with that for free ligand HTTA; the other one at 334 nm, which is assigned to $\pi \rightarrow \pi^*$ transition of the carbonyl group, red-shifts 10 nm and is obviously enhanced in intensity, showing that the carbonyl of HTTA is taken into coordination in the complex.

IR spectra

The IR spectrum of free ligand HTTA has two strong peaks at 1642 and 1661 cm^{-1}, attributable to the stretching vibration of the carbonyl group adjacent to the $—CF_3$ and thienyl groups,[11] respectively. However, in the lanthanum complex, only a single peak is present at a red-shifted wavelength of 1608 cm^{-1}. Also, the $\nu(OH)$ vibration absorption peak at 3400 cm^{-1} due to enol–keto tautomerization of HTTA disappears in the spectrum of the lanthanum complex. These facts suggest that the coordination of lanthanum to carbonyl group oxygen and dissociation of enol hydrogen have taken place and the bond length of C—O tends to be unified. This result was also supported by the crystal structure discussed above. Furthermore, a weak multiplet centred at about 2900 cm^{-1} for the complex and attributed to $\nu(CH_3 + CH_2)$, indicated the presence of N-ethyl.

Thermal analysis

The complex is chemically stable from room temperature to 243°C and melts at 185°C. Over 243°C, it undergoes a series of decomposition and oxidation reactions and finally becomes La_2O_3 at about 556°C. However, the ligand HTTA begins to decompose at 87°C, so the lanthanum complex is thermodynamically more stable than the ligand HTTA.

Tables of anisotropic parameters, atomic coordinates, equations of least square planes and calculated and observed structure factors have been deposited as supplementary materials with the Cambridge Crystallographic Data Centre.

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