SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF COMPLEXES OF RARE EARTH PICRATES WITH *N*,*N*,*N*′,*N*′,*N*″,*N*″-HEXAISOPROPYL- 2,2′,2″-[NITRILO-TRIS(ETHYLENEOXY)]TRIACETAMIDE (L)

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Received October 30, 2001
Accepted March 20, 2002

A new tripodal compound, *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexaisopropyl-2,2′,2″-[nitrilotris(ethyleneoxy)]triacetamide (L) was synthesized. Its complexes with rare earth picrates, $[M(Pic)L](Pic)_2 \cdot H_2O$ (M = La, Pr, Nd, Sm, Eu, Tb, Er, Yb, Y), have been prepared and characterized by elemental analysis, thermal analysis, conductivity measurements, IR and ^1H NMR spectra. The crystal structures of two complexes $[M(Pic)L](Pic)_2$ (M = Sm, Y) have been determined, which reveal that the M(III) ions (M = Sm, Y) are encapsulated by the three chains of the ligand and nine-coordinated by the central nitrogen atom, three ether oxygen atoms and three carbonyl oxygen atoms from the ligand, and two oxygen atoms from the didentate coordinated picrate ion in both cases. The results show that L acts as a heptadentate ligand, forming a cup-like coordination structure to accommodate the rare earth ion. Both rare earth complexes have the similar coordinate modes in spite of different unit cells.

Keywords: Tripodal ligands; Rare earth picrate complexes; Crystal structure determination; Lanthanide complexes; Chelates; Yttrium complex; Samarium complex.

Tripodal compounds are a unique class of complexing agents; they have been extensively used in both coordination and organometallic chemistry fields, probably owing to their easy synthesis, the potential multidentate coordination ability, the ease of structural modification, the unique coordination structures and physical properties of the metal complexes[1–4]. In recent years, the studies on the design and synthesis of their stable rare earth complexes have attracted much attention of scientists in different areas. It is of great importance to note that the rare earth complexes of a 1 : 1 or 1 : 2 or 3 : 2 metal-to-ligand ratio can be obtained through encapsulation of the

doi:10.1135/cccc20020557

rare earth ions in the cavity of those ligands, and may be used as building blocks to construct various two- or three-dimensional supramolecular networks[5]. Moreover, they have unique physical properties and may find potential applications in biology, medicine and materials science[6]. However, the studies on rare earth complexes with tripodal ligands bearing ether-amide arms are very rare. In order to investigate the coordination character and the geometric structures of its rare earth complexes, we report on the synthesis, characterization and crystal structure of the rare earth picrate complexes with a tripodal ligand, *N*,*N*,*N′*,*N′*,*N″*,*N″*-hexaisopropyl-2,2′,2″-[nitrilotris(ethyleneoxy)]triacetamide (see Fig. 1).

RESULTS AND DISCUSSION

Elemental and Thermal Analysis

Analytical data for the complexes (see Table I) conform to a 1 : 3 : 1 metal-to-picrate-to-L stoichiometries, [M(Pic)$_3$L], together with 1 mol of H_2O. All the complexes are soluble in DMSO, DMF, MeCN, $CHCl_3$ and acetone, slightly soluble in ethanol and AcOEt, and sparingly soluble in benzene, Et_2O and cyclohexane. The molar conductivity values of the complexes in MeCN (Table I) indicate the presence of a 2 : 1 electrolyte[7], implying that only one picrate group coordinates to the M(III) ion.

TG and DTA curves of the Sm(III) complex show a weak endothermic peak at *ca* 100 °C and a loss of about 1.6% of its weight, which corresponds

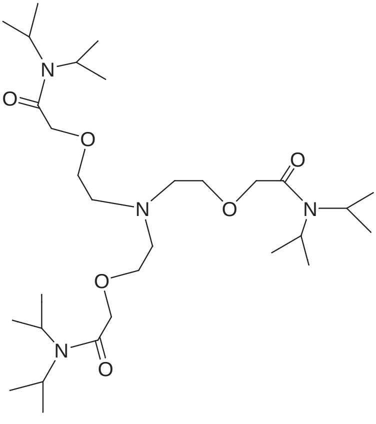

FIG. 1
N,*N*,*N′*,*N′*,*N″*,*N″*-Hexaisopropyl-2,2′,2″-[nitrilotris(ethyleneoxy)]triacetamide (L)

to the loss of one water molecule (calculated H_2O 1.3%). The result is consistent with that of elemental analysis. The complex gradually decomposes with three exothermic peaks at 298, 325 and 480 °C, respectively.

IR Spectra

Selected IR data of L, HPic and the $[M(Pic)L](Pic)_2 \cdot H_2O$ (M = La, Sm, Yb) complexes are given in Table II. The spectra of the complexes show the closely similar vibration.

In the complexes, the C=O bands split into two bands and shift by *ca* 10 and 30 cm^{-1}, respectively, towards lower wavenumbers; at the same time, the C–O–C bands shift also *ca* 15 cm^{-1} towards lower wavenumbers, thus indicating that both the carbonyl oxygen atoms and the ether oxygen atoms take part in coordination to the metal ion[8].

TABLE I
Analytical data for the $[M(Pic)L](Pic)_2 \cdot H_2O$ complexes

Complex	Found (calc.) % C	Found (calc.) % H	Found (calc.) % N	M, %	Λ_m S cm^2 mol^{-1}
$[La(Pic)L](Pic)_2 \cdot H_2O$	40.57 (40.77)	4.79 (4.95)	12.95 (12.88)	9.80 (9.46)	222.5
$[Pr(Pic)L](Pic)_2 \cdot H_2O$	40.98 (40.71)	4.96 (4.84)	13.09 (12.86)	9.69 (9.95)	223.7
$[Nd(Pic)L](Pic)_2 \cdot H_2O$	40.68 (40.62)	4.52 (4.83)	12.66 (12.83)	9.80 (10.16)	215.1
$[Sm(Pic)L](Pic)_2 \cdot H_2O$	40.39 (40.44)	4.69 (4.81)	12.94 (12.78)	10.82 (10.55)	211.3
$[Eu(Pic)L](Pic)_2 \cdot H_2O$	40.25 (40.40)	4.60 (4.80)	12.60 (12.76)	10.37 (10.65)	226.5
$[Tb(Pic)L](Pic)_2 \cdot H_2O$	40.01 (40.20)	4.44 (4.78)	12.58 (12.70)	10.79 (11.08)	216.1
$[Er(Pic)L](Pic)_2 \cdot H_2O$	40.11 (39.96)	4.79 (4.75)	12.77 (12.63)	11.32 (11.59)	243.4
$[Yb(Pic)L](Pic)_2 \cdot H_2O$	39.62 (39.81)	4.69 (4.73)	12.27 (12.51)	11.76 (11.95)	242.1
$[Y(Pic)L](Pic)_2 \cdot H_2O$	41.99 (42.27)	5.10 (5.02)	13.18 (13.35)	6.30 (6.52)	235.2

The OH out-of-plane bending vibration of the HPic at 1 151 cm^{-1} disappears in the spectra of the complexes[9], indicating that the hydrogen atom of the OH group is replaced by M(III). The ν(C-O) vibration at 1 265 cm^{-1} is shifted towards higher wavenumbers by *ca* 5 cm^{-1}. There may be due to the two effects. First, the OH hydrogen atom is replaced by M(III), increasing the π-bond character in the C–O bond. Second, the coordination of the O atom of C–O bond to M(III) causes weakening of the π-bond character. HPic shows $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ at 1 555 and 1 342 cm^{-1}, respectively, which split into two bands at *ca* 1 579 and 1 545 cm^{-1} as well as *ca* 1 364 and 1 335 cm^{-1} in the complexes indicating that some of the nitro O-atoms take part in coordination[8]. The vibration at *ca* 3 440 cm^{-1} is assigned to ν(OH) of water[10].

The close similarity of the complexes in the IR spectra suggests the same coordinating behaviors both of L and of picrates in all cases.

^{1}H NMR spectra

The ^{1}H NMR spectra of the free ligand L and its La(III) complexes were determined in CD_3COCD_3. The chemical shift of L in CD_3COCD_3 is the same as that in $CDCl_3$. In the La(III) complex, the proton signals move to lower field in comparison with L: the signals of the $-CH_2C(O)-$, $-OCH_2-$, NCH_2-

TABLE II
Selected IR data (ν, cm^{-1}) of L, HPic and $[M(Pic)L](Pic)_2 \cdot H_2O$ (M = La, Sm, Yb) complexes

Compound	ν(C=O)	ν(C–O–C)	ν(C–O)	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	ν(OH)
L	1 643	1 118				
HPic			1 265	1 555	1 342	
	1 635			1 579	1 364	
$[La(Pic)L](Pic)_2 \cdot H_2O$		1 103	1 269			3 435
	1 611			1 545	1 335	
	1 634			1 578	1 363	
$[Sm(Pic)L](Pic)_2 \cdot H_2O$		1 102	1 269			3 435
	1 610			1 543	1 334	
	1 636			1 580	1 364	
$[Yb(Pic)L](Pic)_2 \cdot H_2O$		1 105	1 267			3 445
	1 610			1 546	1 335	

protons shift by 0.94, 0.66 and 0.45 ppm, respectively. It suggests that the central nitrogen atom, the ether oxygen atoms and the carbonyl oxygen atoms take part in coordination to the metal ion.

The proton signal of OH group in free HPic disappears in the complex, suggesting that the H atom of the OH group is replaced by M(III). The benzene ring protons of the free HPic exhibit a singlet at 9.12 ppm. Upon coordination, this signal moves to higher field and shifts by 0.37 ppm. Only a singlet is observed for the benzene ring protons of three picrate groups, probably due to fast exchange among the groups in the solution at room temperature[11].

X-Ray Crystal Structure

Figures 2 and 3 show the molecular structures for the samarium and yttrium complexes, respectively. Atomic coordinates and site occupancy factor of all disordered atoms are given in Table III. Selected bond distances and bond angles of the coordination bonds are given in Tables IV and V, respectively.

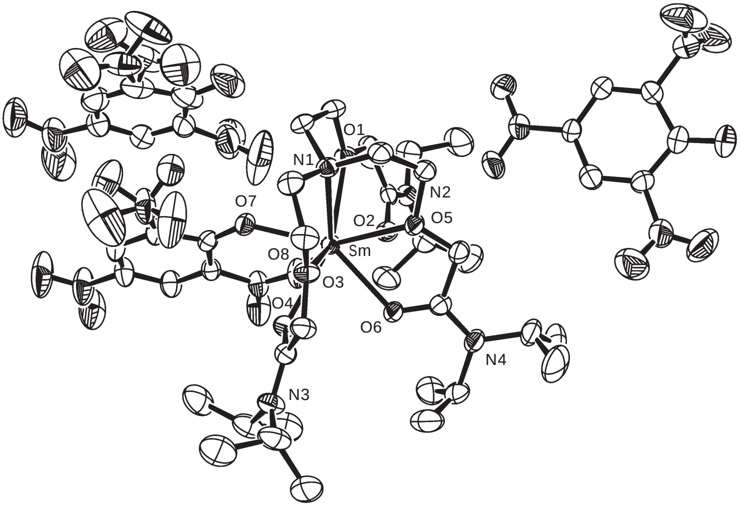

FIG. 2
Molecular structure of the [Sm(Pic)L] $(Pic)_2$ complex with thermal ellipsoids at the 40% probability level. Only the nitrogen atoms of the ligand and the coordinated atoms have been labeled for clarity (some nitro groups are disordered)

The two crystal structures show that both complexes exhibit similar coordinate modes in spite of different unit cells. Each complex is composed of [M(Pic) L](Pic)$_2$ (M = Sm, Y) molecules linked by weak van der Waals forces, although several nitro groups of the picrates in the complexes are poorly defined because of high thermal motion. In the samarium complex, the site occupancy factors of O(12) and O(13) atoms are over twice than that of O(12′) and O(13′) ones, suggesting that the opportunities of site of O(12) and O(13) are much more than that of O(12′) and O(13′) atoms; yet, the site occupancy factors of O(22), N(11) and O(23) atoms are almost equal to that of O(22′), N(11′) and O(23′) ones. In the yttrium complex, the site occupancy factors of O(26) and O(27) atoms are equal to that of O(26′) and O(27′) ones. In a similar way with other rare earth complexes of tripodal ligands[5,6,12], three arms of L stretch around and form a cup-like host to accommodate the metal ion, displaying a tripod-type coordination behavior. The M(III) ions (M = Sm, Y) in the crystals are encapsulated by the three arms of L and nine-coordinated by the central nitrogen atom (N(1)), three ether oxygen atoms (O(1), O(3), O(5)) and three carbonyl oxygen atoms (O(2), O(4), O(6)) of L, and two oxygen atoms (O(7), O(8)) of one didenate picrate.

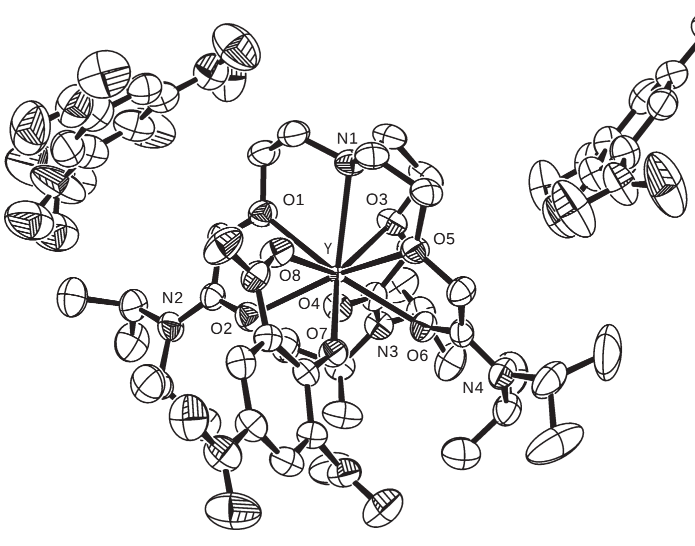

FIG. 3
Molecular structure of the [Y(Pic)L](Pic)$_2$ complex with thermal ellipsoids at the 40% probability level. Only the nitrogen atoms of the ligand and the coordinated atoms have been labeled for clarity

The M–O(7) (phenolic O, Picrate) distances (M = Sm, 0.2331 nm; Y, 0.2290 nm), almost equal to those reported literature[8] (0.2343 nm), are the shortest bond lengths of all bonds between the metal ions and all the coordinated atoms, probably due to a high electron density on the picrate oxygen anion. The M–O(8) (nitro O, Picrate) bond lengths (M = Sm, 0.2495 nm; Y, 0.2454 nm) are slightly shorter than the value in literature[8] (0.2501–0.2778 nm). The average distances of M–O (C=O, L) (M = Sm, 0.2420 nm; Y, 0.2360 nm) in the complexes are a little shorter than those of M–O (C–O–C, L) (M = Sm, 0.2478 nm; Y, 0.2448 nm), showing that the coordination ability of the carbonyl oxygen atom in the ligand is stronger than that of the ether oxygen atom. The distances of M–N(1) (M = Sm, 0.2669 nm; Y, 0.2659 nm) are closely similar to literature value[12b,12d] and

TABLE III
Selected atomic coordinates ($\times 10^{-4}$) and equivalent isotopic displacement parameters ($\times 10^{-5}$ nm^2) for $[M(Pic)L](Pic)_2$ (M = Sm, Y) complexes (U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor)

Atom	*x*	*y*	*z*	U_{eq}	Site occupancy factor
			Samarium complex		
O12	13409(7)	9001(3)	3924(7)	105(3)	0.69
O13	12207(4)	9177(2)	2710(10)	134(5)	0.69
O12′	13430(20)	8951(7)	3210(30)	179(14)	0.31
O13′	12266(9)	9194(3)	3756(14)	75(6)	0.31
N11	13332(15)	9325(3)	6011(17)	83(5)	0.47
O22	12960(20)	9612(5)	6326(18)	142(12)	0.47
O23	14163(9)	9374(4)	5882(15)	143(6)	0.47
N11′	12901(16)	9376(2)	6018(16)	110(5)	0.53
O22′	12309(9)	9596(3)	5462(13)	131(5)	0.53
O23′	13733(14)	9496(4)	6425(12)	119(8)	0.53
			Yttrium complex		
O26	8590(40)	1200(20)	10260(30)	172(11)	0.50
O27	9070(100)	1980(40)	10931(9)	254(16)	0.50
O26′	8250(40)	1730(30)	10250(30)	172(11)	0.50
O27′	9440(100)	1380(50)	10921(11)	254(16)	0.50

much longer than that of M–O, which is in consistent with the theory of soft-hard acid-base.

As a whole, the tripodal compound L acts as a heptadentate ligand in these complexes. Because of its flexibility, three arms can rotate freely around to form a stable cavity of an appropriate size to encapsulate the rare earth ions. This is important for the formation of a host with the coordination atoms ready to uptake a cation.

TABLE IV

Selected bond lengths (in nm) and bond angles (in °) of the [Sm(Pic)L](Pic)$_2$ complex

Bond lengths					
Sm–O1	0.2504(2)	Sm–O2	0.2416(2)	Sm–O3	0.2458(2)
Sm–O4	0.2450(2)	Sm–O5	0.2471(2)	Sm–O6	0.2393(2)
Sm–O7	0.2331(2)	Sm–O8	0.2495(3)	Sm–N1	0.2669(3)
Bond angles					
O1–Sm–N1	62.66(8)	O2–Sm–O1	61.54(8)	O2–Sm–O3	155.06(8)
O2–Sm–O4	121.25(8)	O2–Sm–O5	77.37(8)	O2–Sm–O8	66.31(8)
O2–Sm–N1	116.04(8)	O3–Sm–O1	126.93(7)	O3–Sm–O5	81.34(9)
O3–Sm–O8	129.35(9)	O3–Sm–N1	64.42(8)	O4–Sm–O1	157.13(8)
O4–Sm–O3	61.59(8)	O4–Sm–O5	123.06(8)	O4–Sm–O8	69.90(9)
O4–Sm–N1	122.42(9)	O5–Sm–O1	79.73(8)	O5–Sm–O8	141.30(8)
O5–Sm–N1	64.33(8)	O6–Sm–O1	127.01(8)	O6–Sm–O2	74.53(9)
O6–Sm–O3	84.16(8)	O6–Sm–O4	71.82(8)	O6–Sm–O5	62.24(8)
O6–Sm–O8	94.40(8)	O6–Sm–N1	120.85(8)	O7–Sm–O1	84.03(8)
O7–Sm–O2	118.57(9)	O7–Sm–O3	86.36(9)	O7–Sm–O4	75.03(8)
O7–Sm–O5	147.52(8)	O7–Sm–O6	146.10(8)	O7–Sm–O8	67.31(8)
O7–Sm–N1	83.24(9)	O8–Sm–O1	93.75(9)	O8–Sm–N1	144.48(9)
C1–N1–Sm	105.4(2)	C2–O1–Sm	125.2(2)	C3–O1–Sm	123.62(19)
C4–O2–Sm	126.9(2)	C11–N1–Sm	108.2(2)	C12–O3–Sm	124.9(2)
C13–O3–Sm	120.2(2)	C14–O4–Sm	123.1(2)	C21–N1–Sm	113.5(2)
C22–O5–Sm	118.1(2)	C23–O5–Sm	118.7(2)	C24–O6–Sm	124.4(2)
C31–O7–Sm	139.0(2)	N5–O8–Sm	140.0(2)		

EXPERIMENTAL

Measurements and Materials

The C, H, N elemental analyses were performed using an Elementar Vario EL. The metal ions were determined by EDTA titration using xylenol orange as indicator. The IR spectra (for wavenumbers 400–4000 cm^{-1}) were recorded on a Nicolet AVATAR 360 FT-IR instrument in KBr discs. ^{1}H NMR spectrum was measured on a Bruker AC-80 spectrometer with TMS as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. FAB-MS was measured on a VG ZAB-HS spectrometer. Conductivity measurements

TABLE V
Selected bond lengths (in nm) and bond angles (in °) of the [Y(Pic)L](Pic)$_2$ complex

		Bond lengths			
Y–O1	0.2435(4)	Y–O2	0.2343(4)	Y–O3	0.2441(4)
Y–O4	0.2343(4)	Y–O5	0.2421(4)	Y–O6	0.2396(4)
Y–O7	0.2290(4)	Y–O8	0.2454(4)	Y–N1	0.2658(5)
		Bond angles			
O1–Y–N1	65.01(15)	O1–Y–O3	81.88(15)	O1–Y–O8	76.45(14)
O2–Y–O1	63.17(14)	O2–Y–O3	126.17(15)	O2–Y–O4	72.59(15)
O2–Y–O5	149.22(15)	O2–Y–O6	121.28(15)	O2–Y–O8	74.73(15)
O2–Y–N1	123.47(15)	O3–Y–O8	137.12(14)	O3–Y–N1	64.58(14)
O4–Y–O1	83.20(15)	O4–Y–O3	63.25(14)	O4–Y–O5	132.29(14)
O4–Y–O6	73.26(14)	O4–Y–O8	146.69(16)	O4–Y–N1	121.51(15)
O5–Y–O1	128.29(14)	O5–Y–O3	84.56(15)	O5–Y–O8	80.70(15)
O5–Y–N1	64.08(15)	O6–Y–O1	151.93(15)	O6–Y–O3	74.06(15)
O6–Y–O5	64.15(13)	O6–Y–O8	131.40(14)	O6–Y–N1	114.99(16)
O7–Y–O1	130.97(15)	O7–Y–O2	75.33(15)	O7–Y–O3	146.58(15)
O7–Y–O4	108.98(15)	O7–Y–O5	78.50(15)	O7–Y–O6	72.65(14)
O7–Y–O8	68.10(14)	O7–Y–N1	129.16(15)	O8–Y–N1	72.76(15)
C1–N1–Y	109.3(4)	C2–O1–Y	125.0(4)	C3–O1–Y	119.2(3)
C4–O2–Y	125.0(4)	C11–N1–Y	112.2(3)	C12–O3–Y	117.8(4)
C13–O3–Y	119.8(3)	C14–O4–Y	124.4(4)	C21–N1–Y	106.8(3)
C22–O5–Y	126.1(3)	C23–O5–Y	120.5(3)	C24–O6–Y	122.7(4)
C31–O7–Y	140.9(4)	N5–O8–Y	141.7(4)		

were carried out with a DDSJ-308 conductometer using 10^{-3} M solution in MeCN at 25 °C. Thermal analysis was performed on a Dupont 1090 thermal analyzer in air atmosphere at a heating rate of 10 °C min^{-1}. Crystal structure was measured on a Siemens P4 four-circle diffractometer.

Rare earth picrates[9] and 2-chloro-*N*,*N*-diisopropylacetamide[13] were prepared by literature methods. All solvents were dried prior to use by conventional procedures.

Synthesis of the Ligand (L)

The ligand was prepared by modification of the reported methods[14]. A mixture of triethanolamine (1.5 g, 10 mmol) and NaH (1.0 g, 70%, 30 mmol) was stirred overnight in absolute THF under nitrogen at room temperature. Then, 2-chloro-*N*,*N*-diisopropylacetamide (5.4 g, 30 mmol) in THF was added dropwise and the mixture was refluxed for 72 h. After removal of the solvent, the residue was extracted repeatedly with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated almost to dryness. Chromatography on silica gel with petroleum ether (60–90 °C)–ethyl acetate–ethanol (1 : 2 : 0.1) gave the product, a brown-yellowish viscous liquid, 2.7 g (yield 48%).

^{1}H NMR (80M, $CDCl_3$): 4.05 s, 6 H (-CH_2CO-); 3.59 t, 6 H, *J* = 6 (-CH_2O-); 2.83 t, 6 H, *J* = 6 (NCH_2-); 0.95–1.65 br, 42 H (-N-$(CH(CH_3)_2)_2$). IR: 1 643 (ν(C=O)); 1 118 (ν(C-O-C)). FAB-MS (*m/z*): 573 (M + 1).

General Procedure for Preparation of the Complexes

A 0.1 mM solution of L in ethanol (10 ml) was added dropwise to a 0.1 mM solution of rare earth picrate (M = La, Pr, Nd, Sm, Eu, Tb, Er, Yb, Y) in ethanol (8 ml). The mixture was stirred at room temperature for 6 h. The precipitated solid complex was filtered off, washed and dried *in vacuo* over P_4O_{10} for 48 h. All the complexes were obtained as yellow powders. Their analytical data are given in Table I.

The samarium and yttrium complexes were recrystallized from acetonitrile–ethanol (1 : 1, v/v) by slow evaporation to give transparent yellow crystals suitable for structure determination.

X-Ray Crystallography

For the samarium and yttrium complexes, structure measurements were performed on a Siemens P4 four-circle diffractometer with graphite-monochromatized MoKα radiation (λ = 0.071073 nm). A summary of crystallographic data and details of the structure refinements are listed in Table VI. Empirical absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares technique with all ordered non-hydrogen atoms treated anisotropically. Several nitro groups of the picrates were disordered in the lattice. The hydrogen atoms of the compound were fixed by theoretical models and refined with isotropic factors. All the calculations were performed with the program package Siemens SHELXL97 (ref.[15]).

CCDC 166607 and CCDC 180834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

TABLE VI
Crystallographic data, data collection and structure refinement for the samarium and yttrium complexes

Parameter	[Sm(Pic)L](Pic)$_2$	[Y(Pic)L](Pic)$_2$
Formula	$C_{48}H_{66}N_{13}O_{27}Sm$	$C_{48}H_{66}N_{13}O_{27}Y$
M, g mol^{-1}	1 407.49	1 346.05
Crystal size, mm^3	0.58 × 0.58 × 0.42	0.60 × 0.44 × 0.16
T, K	291(2)	297(2)
Crystal system, space group	monoclinic, $P2_1/c$ (no. 14)	triclinic, P-1 (no. 2)
a, nm; α, °	1.3798(2); 90	1.0535(1); 80.920(10)
b, nm; β, °	3.2747(4); 104.620(10)	1.2478(1); 80.300(10)
c, nm; γ, °	1.4044(2); 90	2.3583(2); 83.230(10)
V, nm^3; Z	6.1402(15); 4	3.0042(5); 2
D, g cm^{-3}	1.523	1.488
F(000); μ, mm^{-1}	2 892; 1.050	1 400; 1.067
θ range, °	1.53–25.00	1.66–25.00
hkl range	0/15, 0/38, –16/16	0/12, –14/14, –27/28
No. of reflections	11 727	11 591
No. of independent reflections	10 661 [R_{int} = 0.0218]	10 585 [R_{int} = 0.0194]
No. of parameters	862	809
R, ωR	0.0341, 0.0758^a	0.0645, 0.1910^b
GOF	0.951	0.990

Weighting scheme: ^{a} $\omega = [\sigma^2(F_o^2) + (0.0426P)^2]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$;
^{b} $\omega = [\sigma^2(F_o^2) + (0.1535P)^2]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$.

This research was supported by the grant from the National Natural Science Foundation of China (No. 29871014).

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