Crystal Structure and Fluorescence Properties of a New Ternary Binuclear Complex: $Sm_2(C_3H_3O_2)_6(phen)_2$

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A new ternary mixed ligand dinuclear samarium(III) complex, $Sm_2(C_3H_3O_2)_6(phen)_2$ (**1**) ($C_3H_3O_2$ = acrylate; phen = 1,10-phenanthroline), has been synthesized and characterized by microanalysis, IR and UV/vis spectra and single crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters: $a = 9.6687(19)$, $b = 10.690(2)$, $c = 10.799(2)$ Å, $\alpha = 105.50(3)$, $\beta = 106.67(3)$, $\gamma = 91.59(3)°$, $V = 1023.8(3)$ Å^3. The Sm(III) cations are bridged by four acrylate anions into a dinuclear molecular unit. The nine-coordinate Sm(III) atoms adopt a significantly distorted monocapped anti-square-prismatic geometry. Within the crystal structure, the complex molecules are associated *via* π-π stacking interactions into one-dimensional supramolecular chains along the [011] direction. Compound **1** exhibits intense fluorescence in the solid state at room temperature.

Key words: Crystal Structure, Binuclear Samarium(III) Complex, Ternary Complex, Fluorescence Properties

Introduction

In the coordination chemistry of the active sites of metalloenzymes, carboxylate groups display a variety of binding geometries, such as monodentate terminal, chelating, bidentate and monodentate bridging modes [1]. A significant number of metal-carboxylate complexes have been prepared and well characterized in an attempt to mimic the fascinating structures of metal-carboxylate clusters and the structural details of the active site(s) that play a role in the mechanisms of catalysis [2 – 11]. Lanthanide ions possess various coordination geometries, and interesting luminescence and magnetic properties, so they can be used to construct unprecedented intriguing structures with special properties useful for materials science of superconductors, magnetic materials, luminescent probes and catalysts [12 – 14]. However, the progress of the chemistry of lanthanide carboxylates has been slow [15], which may be attributed, at least partially, to the tendency of these ions for adopting high coordination numbers that favors the formation of condensed structures and causes difficulties in controlling the synthetic reactions. 2,2-Bipyridine (bpy), 1,10-phenanthroline (phen) and other bidentate chelating ligands have been widely used as substitutes for amino acid side groups in biomimetic chemistry. Acrylatic acid, an O-donor anionic ligand, has been used in the synthesis of several metal carboxylate complexes [16 – 18]. However, there are few reported crystal structures of mixed-ligand lanthanide complexes of acrylato groups and N-heterocycles such as 1,10-phenanthroline, 2,2-bipyridine and 4,4-bipyridine. We present herein the crystal structure and the fluorescence properties of the new ternary samarium(III) mixed-ligand complex $Sm_2(C_3H_3O_2)_6(phen)_2$ (**1**) ($C_3H_3O_2$ = acrylate).

Experimental Section

Measurements of physical properties

All chemicals were commercially available in p. a. grade and used without further purification. The C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer, the UV/vis spectrum was obtained using a Perkin-Elmer Lambda35 analyzer. All excitation and emission spectra were measured with an Aminco Bowman Series 2 instrument with a xenon arc lamp as the excitation light source for the solid samples at r. t.

Table 1. Crystal and refinement data for $Sm_2(C_3H_3O_2)_6$-$(phen)_2$ (**1**).

Formula	$C_{42}H_{34}Sm_2N_4O_{12}$
M_r	1087.43
Crystal size, mm^3	$0.42 \times 0.38 \times 0.36$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	9.6687(19)
b, Å	10.690(2)
c, Å	10.799(2)
α, deg	105.50(3)
β, deg	106.67(3)
γ, deg	91.59(3)
V, $Å^3$	1023.8(3)
Z	2
d_{calcd}, $g\,cm^{-3}$	1.764
$\mu(MoK_\alpha)$, cm^{-1}	2.908
$F(000)$, e	594
hkl range	$-11 \leq h \leq 12$,
	$-13 \leq k \leq 13$,
	$-14 \leq l \leq 14$
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.0299
Refl. measured	10130
Refl. unique	4638
R_{int}	0.023
Param. refined	272
$R(F)/wR2(F^2)^a$ (all reflexions)	0.029/0.074
A, B values for weighting scheme[b]	0.0390, 0.383
GoF $(F^2)^c$	1.196
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	0.97/−0.53

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_c|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$;
[b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, with $P = (F_o^2 + 2F_c^2)/3$;
[c] $GoF(F^2) = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflexions and p is the total number of parameters refined.

*Preparation of $Sm_2(C_3H_3O_2)_6(phen)_2$ (**1**)*

Freshly prepared $Sm(OH)_3$ (0.202 g, 1.0 mmol) was added to a solution of 1,10-phenanthroline monohydrate (0.198 g, 1.0 mmol) and acrylic acid (0.216 g, 3.0 mmol) in 20 mL of C_2H_5OH/H_2O (v/v 1 : 1) with vigorous stirring under reflux conditions for 1 h. The resulting white suspension was filtered and the filtrate was left to stand at r. t. Colorless block-shaped crystals suitable for X-ray diffraction were obtained in 35 % yield after one month. $C_{42}H_{34}Sm_2N_4O_{12}$: calcd. C 46.35, H 3.13, N 5.15; found C 46.38, H 3.18, N 5.12. – IR: ν = 3053m, 1641s, 1619m, 1579vs, 1539s, 1507s, 1494m, 1421s, 1363s, 1267m, 1218w, 1207w, 1140w, 1093w, 1060w, 988m, 960w, 901w, 844s, 767w, 733s, 625w, 554w cm^{-1}.

X-Ray structure analysis

The reflection intensities of **1** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single crystal diffractometer, with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using the $\varphi/2\varphi$ scan mode. Absorption corrections were applied using the pro-

Table 2. Bond lengths (Å) and angles (deg) for **1**.

Sm1–N1	2.610(3)	Sm1–O6	2.626(3)
Sm1–N2	2.642(3)	O1–C13	1.253(5)
Sm1–O1	2.455(3)	O2–C13	1.253(5)
Sm1–O2	2.508(3)	O3–C16	1.258(4)
Sm1–O3	2.380(3)	O4–C16	1.254(4)
Sm1–O4#1	2.373(2)	O5–C19	1.230(5)
Sm1–O5	2.528(3)	O6–C19	1.267(4)
Sm1–O6#1	2.379(3)	Sm1–Sm1#1	3.988(1)
N1–Sm1–O6	119.14(9)	O1–Sm1–O4#1	78.92(1)
N1–Sm1–N2	62.36(9)	O2–Sm1–O4#1	126.80(1)
O1–Sm1–O2	52.37(9)	O3–Sm1–O4#1	135.92(9)
O1–Sm1–O5	142.02(1)	O5–Sm1–O4#1	85.84(1)
O1–Sm1–O6	146.02(9)	O4#1–Sm1–O6#1	74.36(9)
O1–Sm1–N1	93.32(1)	O6–Sm1–O4#1	70.01(9)
O1–Sm1–N2	72.09(1)	N1–Sm1–O4#1	139.13(9)
O2–Sm1–O5	145.44(9)	N2–Sm1–O4#1	77.19(9)
O2–Sm1–O6	144.02(9)	O5–Sm1–N1	75.94(1)
O2–Sm1–N1	71.37(1)	O5–Sm1–N2	70.67(9)
O2–Sm1–N2	102.78(1)	O5–Sm1–O6	50.18(8)
O3–Sm1–O1	129.59(1)	O1–Sm1–O6#1	84.43(1)
O3–Sm1–O2	78.47(1)	O2–Sm1–O6#1	80.32(9)
O3–Sm1–O5	84.69(1)	O3–Sm1–O6#1	76.16(1)
O3–Sm1–O6	70.97(9)	O5–Sm1–O6#1	124.60(9)
O3–Sm1–N1	79.03(9)	O6–Sm1–O6#1	74.42(1)
O3–Sm1–N2	137.83(9)	N1–Sm1–O6#1	145.42(1)
Sm1–O6–Sm1#1	105.58(1)	N2–Sm1–O6#1	146.00(9)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $2-y$, $1-z$.

gram SADABS [19]. The structure was solved by Direct Methods (SHELXS-97 [20]) and refined by full-matrix least-squares methods on F^2 (SHELXL-97 [21]). The hydrogen atoms associated with carbon atoms were generated geometrically. All non-hydrogen atoms were finally refined with anisotropic displacement parameters, and hydrogen atoms included with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 629380 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Structure description

The asymmetric unit of compound **1** contains one Sm^{3+} cation, three acrylate anions and one phenanthroline ligand. Of the three crystallographically distinct acrylate anions, one functions as a bidentate chelating, one as both a bidentate bridging and bidentate chelating, and one as a monobridging ligand, respectively (Fig. 1). The Sm(III) atom is surrounded by
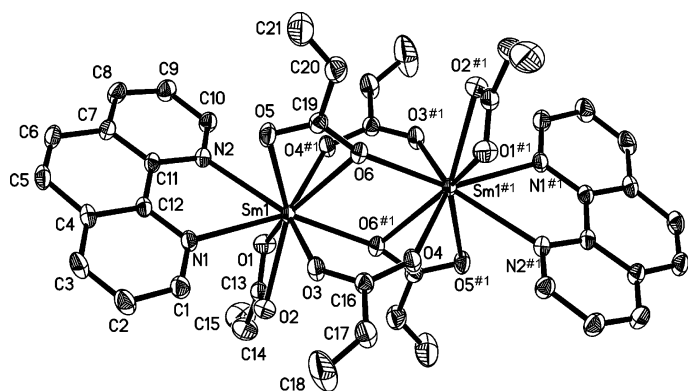
Fig. 1. ORTEP drawing of the molecular structure of **1**, showing 30 % probability displacement ellipsoids and the atom labeling scheme. For the sake of clarity, H atoms have been omitted (symmetry code: [#1] $1-x$, $1-y$, $1-z$).
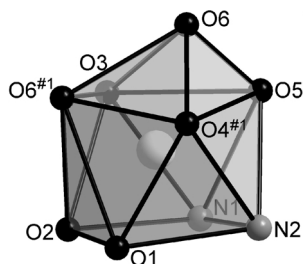

Fig. 2. The monocapped anti-square-prismatic geometry of the SmN_2O_7 core of **1**.

Fig. 3. UV/vis spectrum of **1** in DMF.

two N atoms of one 1,10-phenanthroline ligand and seven O atoms of five acrylate ligands to form a significantly distorted SmN_2O_7 monocapped anti-square-prismatic geometry, with the O6 atom occupying the capping position (Fig. 2). The Sm–N1 bond length (2.610(3) Å) is slightly shorter than the Sm–N2 bond length (2.642(3) Å), both of which are within the range of those observed for other nine-coordinate Sm(III) complexes with nitrogen donor ligands [22]. The Sm–O bond lengths range from 2.373(2) to 2.626(3) Å, with an average distance of 2.403(2) Å, which are comparable to those in related Sm(III)-carboxylates [22 – 23]. The other geometrical details of the acrylate and 1,10-phenanthroline groups are within the normal range (Table. 2) [16 – 18, 22 – 23]. Remarkably, the Sm atoms are bridged by two pairs of acrylato ligands to generate centrosymmetric dinuclear molecules $[Sm_2(C_3H_3O_2)_6(phen)_2]$ with a Sm–Sm separation of 3.9884(12) Å.

In the crystal structure, the molecular packing appears to be influenced by π-π stacking interactions between parts of the 1,10-phenanthroline ring systems of neighboring molecules, with a mean interplanar distance of 3.389(1) Å; the distance between the centroids of the C1–C6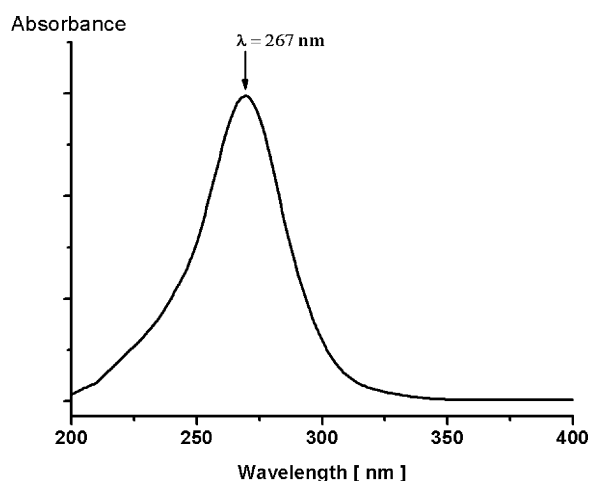, C11, C12, N1 ring and its symmetry-equivalent ($-x$, $1-y$, $-z$) is 3.74 Å. The π-π stacking interactions lead to a one-dimensional chain along the [011] direction.

IR and UV/vis spectra

The infrared spectrum of compound **1** shows the unsaturated ν(=C-H) stretching vibration at 3053 cm^{-1}. The absorptions at 1641 and 1363 cm^{-1} can be assigned to the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching vibrations. A comparison with the characteristic carboxylate stretching vibrations of free acrylatic acid shows a significant blue-shift due to the coordination interactions. The phen-based absorptions (1619, 1579, 1539, 1507, 844, 733 and 625 cm^{-1}) are characteristic of the chelating form of the ligand [24].

An UV/vis spectral measurement was carried out at r. t. on samples dissolved in DMF. The spectrum exhibits a broad absorption band with the maximum at
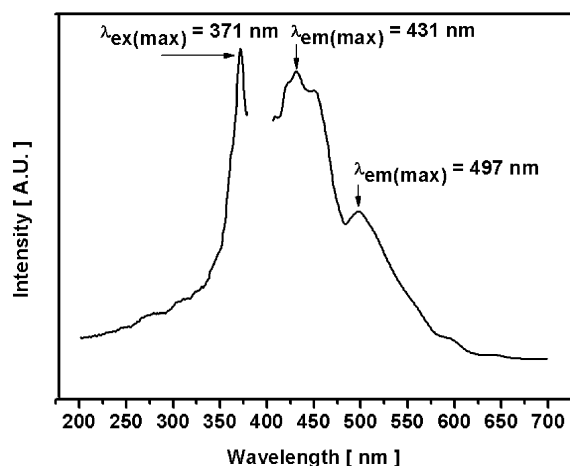
Fig. 4. Fluorescence spectrum of **1** in the solid state at r. t.

ca. 267 nm, which can be assigned to the 1,10-phenan-throline $\pi \rightarrow \pi^*$ transitions (Fig. 3).

Fluorescence properties

The solid-state fluorescence spectrum of **1** at r. t. is depicted in Fig. 4. Complex **1** exhibits intense blue fluorescence with an emission maximum at *ca.* 431 and a weak peak at *ca.* 497 nm upon the maximal excitation at *ca.* 371 nm (Fig. 4). The free 1,10-phenanthroline displays a weak luminescence at *ca.* 365 nm in the solid state at r. t. The fluorescence enhancement in **1** may be due to both coordination and crystal packing interactions. The fluorescence red-shift of the emission energy from the free ligand to the complex appears to be related to the phen-phen π-π stacking interactions, which result in a decrease in the HOMO-LUMO energy gap of the complex [25].

Acknowledgement

[1] G. B. Deacon, R. Philips, *Coord. Chem. Rev.* **1980**, *88*, 227 – 250.
[2] P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625 – 3648.
[3] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504 – 1518.
[4] G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762 – 1765.
[5] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469 – 472.
[6] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350 – 1354.
[7] E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374 – 6381.
[8] K. Hanson, N. Calin, D. Bugaris, M. Scancella, S. C. Sevov, *J. Am. Chem. Soc.* **2004**, *126*, 10502 – 10503.
[9] D. W. Smithenry, S. R. Wilson, K. S. Suslick, *Inorg. Chem.* **2003**, *42*, 7719 – 7721.
[10] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375.
[11] C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490 – 1521; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466 – 1496.
[12] J. Ballato, J. S. Lewis, P. Holloway, *Mater. Res. Soc. Bull.* **1999**, *24*, 51 – 56.
[13] A. J. Steckl, J. M. Zavada, *Mater. Res. Soc. Bull.* **1999**, *24*, 33 – 38.
[14] M. Bredol, U. Kynast, C. Ronda, *Adv. Mater.* **1991**, *3*, 361 – 367.

[15] L. Pan, K. M. Adams, H. E. Hernandez, X. T. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* **2003**, *125*, 3062 – 3067.
[16] G. Kickelbick, P. Wiede, U. Schubert, *Inorg. Chim. Acta* **1999**, *284*, 1 – 7.
[17] S. Jana, D. C. Sherrington, *Angew. Chem.* **2005**, *117*, 4882 – 4886; *Angew. Chem. Int. Ed.* **2005**, *44*, 4804 – 4808.
[18] B. Moraru, N. Husing, G. Kickelbick, U. Schubert, P. Fratzl, H. Peterlik, *Chem. Mater.* **2002**, *14*, 2732 – 2740.
[19] G. M. Sheldrick, Sadabs, University of Göttingen, Göttingen (Germany) **2003**.
[20] G. M. Sheldrick, Shelxs-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
[21] G. M. Sheldrick, Shelxl-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
[22] S.-Y. Niu, J. Jin, Z.-Z. Yang, G.-D. Yang, W.-M. Bu, L. Yie, *Synth. React. Inorg. Met.-Org. Chem.* **2000**, *30*, 777 – 790.
[23] L. Jongen, C. Bromant, D. Hinz-Hubner, G. Meyer, K. Robeyns, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Z. Anorg. Allg. Chem.* **2003**, *629*, 975 – 980.
[24] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Ed., Wiley, New York, **1978**.
[25] H. Yersin, A. Vogler, *Photochemistry and Photophysics of Coordination Compounds*, Springer, Berlin, **1987**.