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Crystal structure of di(3,5-dinitrobenzoato-*O*,*O′*)tetra(μ-3,5-dinitrobenzoato-*O*,*O′*) di(1,10-phenanthroline-*N*,*N′*)dieuropium(III), $Eu_2(C_7H_3N_2O_6)_6(C_{12}H_8N_2)_2$

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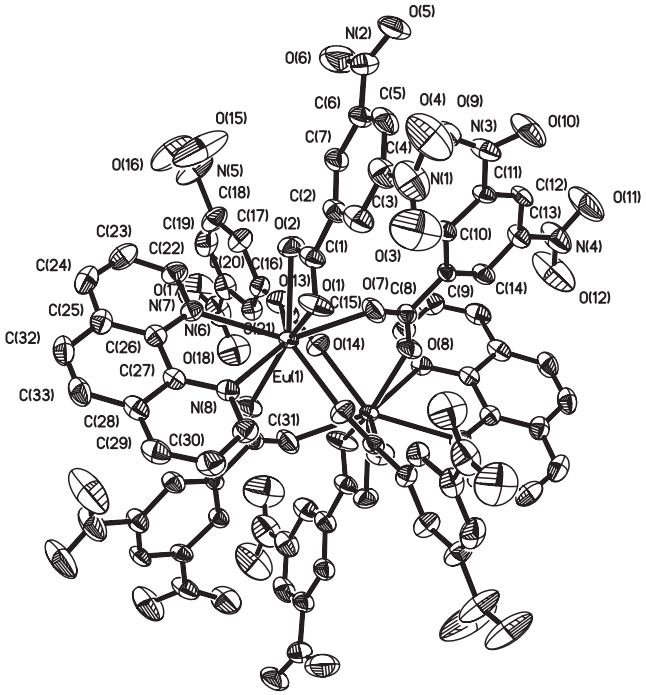

Abstract

$C_{66}H_{34}Eu_2N_{16}O_{36}$, monoclinic, $P12_1/n1$ (No. 14), $a = 11.889(2)$ Å, $b = 22.660(4)$ Å, $c = 13.491(2)$ Å, $\beta = 101.710(2)°$, $V = 3558.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.064$, $T = 293$ K.

Source of material

The title complex was synthesized by the hydrothermal method from a mixture of 3,5-dinitrobenzoic acid (0.6 mmol), $Eu(ClO_4)_3 \cdot 6H_2O$ (0.1 mmol), 1,10-phenanthroline (1.5 mmol) and water (20.0 mL) in a 30.0 mL Teflon-lined stainless steel reactor. The solution was heated to 415 K for three days. After the reaction system was slowly cooled to room temperature, the prismatic colorless crystals were collected and washed with distilled water. The yield is ca. 35% based on Eu(III). The substance is insoluble in water and common organic solvents.

Discussion

In recent years, considerable efforts to novel rare earth complexes have been actively made, owing to their intriguing structural diversity, coordination modes and optical, electronic, magnetic, biological properties [1-3]. Furthermore, lanthanide ions are well known for the variable coordination number from 3 to 12 and carboxylate anions possess versatile binding modes such as monodentate, chelating bidentate, bridging bidentate and bridging tridentate in some lanthanide complexes [4], so the above anions and ions have been widely utilized in preparing many kinds of structures. Herein, we report on a new dimeric complex of europium(III), namely, $Eu_2(C_7H_3N_2O_6)_6(C_{12}H_8N_2)_2$.

The title complex comprises two Eu(III) ions, four bridging 3,5-dinitrobenzoato anions, two chelating 3,5-dinitrobenzoato anions and two 1,10-phenantholine molecules. The coordination of the Eu(III) ion can be described as a square antiprism. The complex is a dimer with a Eu-Eu separation of 4.4266(7) Å and a center of symmetry. The coordination involves six oxygen atoms from five 3,5-dinitrobenzoato anions and two nitrogen atoms from one 1,10-phenthanoline molecule. The six 3,5-dinitrobenzoato anions in the dimeric complex show two coordination modes: one mode bonds to two Eu(III) ions through O7, O8, O13 and O14 in the range 2.328(2) Å to 2.362(2) Å; the other mode is chelated to one Eu(III) ion with distances of 2.456(2) Å and 2.444(2) Å for O1—Eu and O2—Eu, respectively. It should be noted that the π-π stacking interactions play an important role in the crystal structure of the title complex, as shown in bottom figure: The two phenanthroline rings from neighboring dimeric unit are parallel to each other and results in significant π-π stacking. The interplanar distance between the two planes is about 3.42 Å. Meanwhile, there are also π-π stacking interactions between 3,5-dinitrobenzoato rings with the distance of 3.50 Å. Then, an extended three-dimensional network structure with π-π stacking between 1,10-phenanthroline rings and between 3,5-dinitrobenzoato rings is formed.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.35 × 0.48 × 0.65 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.58 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, 860 frames, $\Delta\omega = 2°$
$2\theta_{max}$:	55.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21091, 7993
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6450
$N(param)_{refined}$:	609
Programs:	SHELX-97 [5], ORTEP-II [6]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	1.263(3)	0.338(2)	0.704(3)	0.05(1)
H(2)	4*e*	1.267(3)	0.159(2)	0.720(2)	0.043(9)
H(3)	4*e*	1.013(3)	0.248(2)	0.799(3)	0.05(1)
H(4)	4*e*	1.174(2)	0.308(1)	1.004(2)	0.028(8)
H(5)	4*e*	1.303(3)	0.219(1)	1.250(2)	0.034(9)
H(6)	4*e*	1.185(3)	0.380(2)	1.274(3)	0.05(1)
H(7)	4*e*	0.684(3)	0.353(1)	0.948(2)	0.031(9)
H(8)	4*e*	0.403(3)	0.384(2)	1.047(3)	0.06(1)
H(9)	4*e*	0.668(2)	0.494(1)	1.119(2)	0.021(7)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10)	4*e*	0.730(3)	0.391(1)	0.778(2)	0.038(9)
H(11)	4*e*	0.565(3)	0.384(2)	0.655(3)	0.06(1)
H(12)	4*e*	0.553(3)	0.435(2)	0.502(3)	0.06(1)
H(13)	4*e*	0.977(3)	0.612(2)	0.456(3)	0.05(1)
H(14)	4*e*	1.137(3)	0.612(2)	0.585(2)	0.05(1)
H(15)	4*e*	1.134(3)	0.553(1)	0.726(2)	0.029(8)
H(16)	4*e*	0.624(3)	0.505(2)	0.402(3)	0.05(1)
H(17)	4*e*	0.779(3)	0.571(2)	0.381(3)	0.06(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu(1)	4*e*	0.98424(1)	0.459189(6)	0.84875(1)	0.02469(8)	0.01817(8)	0.02267(7)	0.00059(6)	0.00926(5)	0.00057(6)
N(1)	4*e*	1.3899(3)	0.2484(2)	0.6676(3)	0.068(3)	0.080(3)	0.078(3)	0.029(2)	0.032(2)	0.005(2)
N(2)	4*e*	1.0909(3)	0.1412(1)	0.7916(2)	0.067(2)	0.032(2)	0.059(2)	–0.002(2)	–0.006(2)	–0.008(1)
N(3)	4*e*	1.2640(3)	0.2062(1)	1.0585(2)	0.083(2)	0.026(2)	0.032(2)	0.012(2)	0.017(2)	0.002(1)
N(4)	4*e*	1.2760(4)	0.2930(2)	1.3903(2)	0.115(3)	0.057(2)	0.029(2)	0.035(2)	0.008(2)	0.005(2)
N(5)	4*e*	0.4857(4)	0.3046(2)	0.9403(3)	0.065(3)	0.096(3)	0.086(3)	–0.050(2)	0.025(2)	–0.033(2)
N(6)	4*e*	0.4586(3)	0.4797(2)	1.1479(3)	0.039(2)	0.071(2)	0.062(2)	0.016(2)	0.026(2)	0.013(2)
N(7)	4*e*	0.8045(2)	0.4492(1)	0.7073(2)	0.030(1)	0.030(1)	0.030(1)	–0.005(1)	0.010(1)	–0.001(1)
N(8)	4*e*	0.9852(2)	0.5184(1)	0.6848(2)	0.033(1)	0.028(1)	0.025(1)	–0.002(1)	0.011(1)	0.002(1)
O(1)	4*e*	1.1186(2)	0.40598(9)	0.7645(2)	0.069(2)	0.025(1)	0.054(1)	0.010(1)	0.040(1)	0.006(1)
O(2)	4*e*	0.9768(2)	0.35472(9)	0.8028(2)	0.042(1)	0.028(1)	0.054(1)	0.002(1)	0.009(1)	–0.013(1)
O(3)	4*e*	1.4343(3)	0.2951(2)	0.6596(3)	0.087(3)	0.093(3)	0.170(4)	0.000(2)	0.071(3)	0.004(3)
O(4)	4*e*	1.4275(3)	0.2009(2)	0.6495(3)	0.099(3)	0.098(3)	0.128(3)	0.057(2)	0.062(2)	0.012(2)
O(5)	4*e*	1.1499(3)	0.0971(1)	0.7956(2)	0.096(2)	0.028(1)	0.072(2)	0.015(1)	–0.001(2)	–0.002(1)
O(6)	4*e*	0.9958(3)	0.1413(1)	0.8105(3)	0.066(2)	0.046(2)	0.155(3)	–0.012(2)	0.016(2)	0.010(2)
O(7)	4*e*	1.0996(2)	0.4096(1)	0.9867(2)	0.059(2)	0.036(1)	0.036(1)	0.011(1)	0.001(1)	0.011(1)
O(8)	4*e*	1.1068(2)	0.45124(9)	1.1364(2)	0.040(1)	0.025(1)	0.051(1)	0.0100(9)	0.015(1)	–0.000(1)
O(9)	4*e*	1.1997(3)	0.1985(1)	0.9784(2)	0.128(3)	0.041(2)	0.042(2)	0.013(2)	–0.001(2)	–0.014(1)
O(10)	4*e*	1.3459(3)	0.1752(1)	1.0910(2)	0.115(3)	0.054(2)	0.059(2)	0.054(2)	0.021(2)	–0.002(1)
O(11)	4*e*	1.3154(4)	0.2469(1)	1.4272(2)	0.168(4)	0.066(2)	0.039(2)	0.052(2)	0.004(2)	0.014(2)
O(12)	4*e*	1.2572(4)	0.3349(2)	1.4387(2)	0.246(5)	0.084(3)	0.034(2)	0.083(3)	0.016(2)	–0.008(2)
O(13)	4*e*	0.8489(2)	0.4286(1)	0.9444(2)	0.042(1)	0.038(1)	0.043(1)	–0.005(1)	0.025(1)	0.004(1)
O(14)	4*e*	0.8645(2)	0.4764(1)	1.0908(2)	0.032(1)	0.042(1)	0.044(1)	–0.011(1)	0.007(1)	–0.003(1)
O(15)	4*e*	0.5405(4)	0.2768(2)	0.8919(4)	0.109(3)	0.140(4)	0.209(5)	–0.067(3)	0.071(3)	–0.117(4)
O(16)	4*e*	0.3891(3)	0.2925(2)	0.9476(3)	0.083(3)	0.133(3)	0.127(3)	–0.076(2)	0.036(2)	–0.037(3)
O(17)	4*e*	0.3631(3)	0.4644(2)	1.1541(3)	0.048(2)	0.109(3)	0.145(3)	0.004(2)	0.059(2)	–0.002(2)
O(18)	4*e*	0.5043(3)	0.5245(2)	1.1856(3)	0.067(2)	0.078(2)	0.090(2)	0.012(2)	0.038(2)	–0.015(2)
C(1)	4*e*	1.0707(3)	0.3579(1)	0.7742(2)	0.056(2)	0.025(2)	0.027(2)	0.007(2)	0.011(2)	0.001(1)
C(2)	4*e*	1.1279(3)	0.3013(1)	0.7535(2)	0.052(2)	0.029(2)	0.027(2)	0.012(2)	0.006(1)	–0.004(1)
C(3)	4*e*	1.2285(4)	0.3018(2)	0.7172(3)	0.063(3)	0.039(2)	0.044(2)	0.011(2)	0.017(2)	0.003(2)
C(4)	4*e*	1.2804(3)	0.2485(2)	0.7040(3)	0.055(2)	0.047(2)	0.046(2)	0.017(2)	0.016(2)	–0.001(2)
C(5)	4*e*	1.2374(4)	0.1957(2)	0.7267(3)	0.065(3)	0.037(2)	0.039(2)	0.025(2)	0.004(2)	–0.006(2)
C(6)	4*e*	1.1371(3)	0.1970(1)	0.7620(2)	0.054(2)	0.026(2)	0.039(2)	0.007(2)	–0.002(2)	–0.005(1)
C(7)	4*e*	1.0812(3)	0.2485(2)	0.7759(2)	0.046(2)	0.032(2)	0.037(2)	0.008(2)	0.002(2)	–0.004(1)
C(8)	4*e*	1.1218(2)	0.4094(1)	1.0809(2)	0.022(2)	0.025(2)	0.037(2)	0.003(1)	0.007(1)	0.002(1)
C(9)	4*e*	1.1723(2)	0.3538(1)	1.1319(2)	0.021(1)	0.022(2)	0.031(2)	0.003(1)	0.007(1)	0.002(1)
C(10)	4*e*	1.1892(3)	0.3054(1)	1.0735(2)	0.036(2)	0.027(2)	0.025(2)	0.003(1)	0.007(1)	0.002(1)
C(11)	4*e*	1.2400(3)	0.2557(1)	1.1213(2)	0.044(2)	0.020(2)	0.028(2)	0.005(1)	0.011(1)	–0.002(1)
C(12)	4*e*	1.2716(3)	0.2505(1)	1.2240(2)	0.042(2)	0.023(2)	0.037(2)	0.011(1)	0.006(1)	0.007(1)
C(13)	4*e*	1.2478(3)	0.2982(1)	1.2793(2)	0.050(2)	0.034(2)	0.024(2)	0.010(2)	0.009(1)	0.002(1)
C(14)	4*e*	1.2008(3)	0.3497(1)	1.2359(2)	0.041(2)	0.026(2)	0.035(2)	0.009(1)	0.010(1)	–0.003(1)
C(15)	4*e*	0.8134(3)	0.4449(1)	1.0203(2)	0.027(2)	0.025(2)	0.032(2)	–0.002(1)	0.010(1)	0.008(1)
C(16)	4*e*	0.6949(2)	0.4249(1)	1.0293(2)	0.025(2)	0.035(2)	0.027(2)	–0.006(1)	0.009(1)	0.003(1)
C(17)	4*e*	0.6461(3)	0.3747(2)	0.9811(2)	0.038(2)	0.048(2)	0.031(2)	–0.011(2)	0.013(2)	–0.005(2)
C(18)	4*e*	0.5367(3)	0.3591(2)	0.9902(3)	0.044(2)	0.057(2)	0.042(2)	–0.024(2)	0.010(2)	–0.003(2)
C(19)	4*e*	0.4725(3)	0.3926(2)	1.0431(3)	0.029(2)	0.071(3)	0.051(2)	–0.012(2)	0.010(2)	0.012(2)
C(20)	4*e*	0.5228(3)	0.4423(2)	1.0897(2)	0.029(2)	0.053(2)	0.039(2)	0.004(2)	0.015(1)	0.009(2)
C(21)	4*e*	0.6331(3)	0.4589(2)	1.0846(2)	0.028(2)	0.039(2)	0.033(2)	–0.001(1)	0.010(1)	0.004(1)
C(22)	4*e*	0.7173(3)	0.4150(2)	0.7161(3)	0.042(2)	0.039(2)	0.040(2)	–0.011(2)	0.012(2)	–0.000(2)
C(23)	4*e*	0.6194(3)	0.4081(2)	0.6413(3)	0.036(2)	0.056(2)	0.055(2)	–0.018(2)	0.014(2)	–0.011(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(24)	4*e*	0.6106(3)	0.4389(2)	0.5536(3)	0.033(2)	0.057(2)	0.044(2)	–0.001(2)	0.001(2)	–0.013(2)
C(25)	4*e*	0.6992(3)	0.4768(1)	0.5404(2)	0.032(2)	0.040(2)	0.034(2)	0.005(1)	0.006(1)	–0.005(1)
C(26)	4*e*	0.7957(3)	0.4802(1)	0.6195(2)	0.032(2)	0.029(2)	0.027(2)	0.004(1)	0.010(1)	–0.004(1)
C(27)	4*e*	0.8910(3)	0.5174(1)	0.6088(2)	0.032(2)	0.026(2)	0.025(1)	0.004(1)	0.012(1)	0.001(1)
C(28)	4*e*	0.8828(3)	0.5516(1)	0.5197(2)	0.052(2)	0.032(2)	0.025(2)	0.009(2)	0.016(1)	0.004(1)
C(29)	4*e*	0.9769(3)	0.5872(2)	0.5121(3)	0.060(2)	0.037(2)	0.035(2)	0.000(2)	0.021(2)	0.010(2)
C(30)	4*e*	1.0699(3)	0.5882(2)	0.5882(2)	0.050(2)	0.042(2)	0.038(2)	–0.010(2)	0.018(2)	0.005(2)
C(31)	4*e*	1.0711(3)	0.5527(2)	0.6736(3)	0.037(2)	0.039(2)	0.036(2)	–0.007(2)	0.011(2)	0.002(1)
C(32)	4*e*	0.6956(3)	0.5112(2)	0.4511(2)	0.044(2)	0.051(2)	0.031(2)	0.013(2)	–0.003(2)	–0.002(2)
C(33)	4*e*	0.7829(3)	0.5463(2)	0.4413(2)	0.054(2)	0.048(2)	0.027(2)	0.011(2)	0.004(2)	0.007(2)

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References

1. Hu, M. L.; Huang, Z. Y.; Cheng, Y. Q. ; Wang, S.; Lin, J. J.; Hu, Y.; Xu, D. J.; Xu, Y. Z.: Crystal structure and fluorescence spectrum of the complex [Eu(III)$(TTA)_3$(phen)]. Chin. J. Chem. **17** (1999) 637-643.
2. Niu, S. Y.; Yang, Z. Z.; Yang, Q. C.; Yang, B.; Chao, J. Q.; Yang, G. D.; Shen, E. Z.: Structure and magnetism of tetraacetato bridged binuclear Nd(III) complex. Polyhedron **16** (1997) 1629-1635.
3. Li, X.; Jin, L. P.; Zheng, X. J.; Lu, S. Z.; Zhang, J. H.: Synthesis, structure and luminescence property of the three ternary and quaternary europium complexes. J. Mol. Struct. **607** (2002) 59-67.
4. Zhang, D. L.; Huang, C. H.; Xu, G. X.: Structural studies on rare earth carboxylates I. studies on the crystal structure of tris(neopentanoato)-tris(neopentanoic acid)neodymium(III) dimer, $[NdA_3(HA)_3]_2$. Chin. J. Chem. **8** (1990) 529-535.
5. Sheldrick, G. M.: SHELX-97. Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany 1997.
6. Johnson, C. K.: ORTEP-II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA 1976.