



CRYSTAL STRUCTURE AND SPECTRA OF COMPLEX [Eu(*o*-ABA)₃bipy]bipy

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(Received 22 November 1995; accepted 15 February 1996)

Abstract—[Eu(*o*-ABA)₃bipy]bipy (where *o*-ABA = *o*-aminobenzoate and bipy = 2,2'-bipyridine) was synthesized and characterized by X-ray diffraction, IR and Raman spectra. In the crystal the compound exists as a dimer, each europium atom is eight-coordinated and has one bipyridine molecule, one bidentate carboxylate group and four oxygen atoms from bridging carboxylates. Luminescence data show that the complex contains one Eu^{III} ion in a site with low symmetry. Copyright © 1996 Elsevier Science Ltd

Many types of lanthanide carboxylates have been reported. The carboxylates show interesting polymeric network and chain structures.¹ However, to our knowledge only a few lanthanide carboxylates fluoresce. Recently we have studied crystal structures and characteristic luminescence of the europium complexes with aromatic acids and nitrogen-containing ligands.^{2–7} During the course of our work with a variety of the europium complexes, we have found that flexibility of bipy is of importance in explaining europium ion sites in the excited state. In extending our investigation of structures and luminescence, we report here the results of an X-ray structure and spectra on the [Eu(*o*-ABA)₃bipy]bipy complex.

EXPERIMENTAL

*Synthesis of [Eu(*o*-ABA)₃bipy]bipy*

o-HABA (1.5 mmol) and bipy (0.5 mmol) were dissolved in 50% C₂H₅OH (25 cm³). To the result-

ing clear solution was added EuCl₃ solution (0.5 mmol dissolved in 10 cm³ 50% C₂H₅OH) dropwise and the reaction left to stir for 8 h. A single crystal was obtained from the saturated solution.

Crystal structure determination

Crystal system, accurate cell constants, space group and intensity data were obtained from single crystal mounted on an Enraf–Nonius CAD-4 X-ray diffractometer using graphite monochromated Mo-*K*_α radiation. Data were collected by an ω -2 θ scan technique for $2 < \theta < 23^\circ$ with indices in the range $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $0 \leq l \leq 17$ and were corrected for Lorentz–polarization and absorption effects. All calculations were performed with SDP-PLUS, SHELXS-86 and SHELXL-93 programs on PDP 11/44 and IBM 486. The structure of [Eu(*o*-ABA)₃bipy]bipy was solved by direct methods and refined with the full-matrix least-squares technique to $R = 0.031$, $R_w = 0.038$. A summary of the crystallographic data and data collection and refinement parameters is given in Table 1.

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Table 1. Experimental details

Chemical formula	C ₈₂ H ₆₈ Eu ₂ N ₁₄ O ₁₂
Color	Dark brown
Crystal size (mm)	0.2 × 0.2 × 0.3
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (nm)	1.1327(3)
<i>b</i> (nm)	1.1474(4)
<i>c</i> (nm)	1.5791(5)
α (°)	73.45(2)
β (°)	77.31(2)
γ (°)	70.46(1)
<i>V</i> (Å ³)	1836.31(9)
<i>Z</i>	1
<i>M</i>	1745.46
<i>D</i> ₀ (mg mm ⁻³)	1.58
Absorption coefficient (mm ⁻¹)	1.767
<i>F</i> (000)	880
λ (Å) (Mo- <i>K</i> _α)	0.71073
Temperature (K)	299 ± 1
θ range (°)	2.0–23.0
Scan speed (° min ⁻¹)	0.92–5.49
Reflections collected	5325
Independent reflections	4885 (<i>R</i> _m = 2.00%)
Observed reflections	4690 [<i>I</i> ≥ 3σ(<i>I</i>)]
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Number of parameters refined	496
Final <i>R</i> and <i>R</i> _w	0.031 and 0.038
Weighting scheme	w = 1 for all of observed reflections
Goodness-of-fit	1.89
Maximum Δ/σ	1.0
Max. residual peak (e Å ⁻³)	0.92

Spectral determination

The IR spectrum of [Eu(*o*-ABA)₃bipy]bipy was recorded on a Nicolet FT-IR 170 SX spectrometer. The Raman spectrum for the complex was measured on 910 FT-Raman spectrometer. Luminescence measurement was given in ref. 5.

RESULTS AND DISCUSSION

The molecular structure and atomic numbering of the complex and crystal packing are shown in Figs 1 and 2, respectively. The bond distances and angles are listed in Tables 2 and 3. The dinuclear entity is centrosymmetric, with four bridging carboxyl groups. Each europium atom is linked to eight atoms, four oxygen atoms from the bridging carboxylates, two oxygen atoms from a chelating carboxylate group and two nitrogen atoms from a bipyridine molecule. A notable feature of the crystal packing includes two bipyridine molecules, not bonded to the europium atoms. The two Eu—O [Eu—O(1) and Eu—O(3)] bond lengths on the one

side of the Eu—Eu(a) are slightly longer than the two Eu—O [Eu—O(2) and Eu—O(4a)] bond distances on the other side due to the larger steric effect of the bipy ligand. Comparison of the crystal structure of [Eu(*o*-ABA)₃bipy]bipy with that of the europium *p*-aminobenzoate complex with 2,2'-bipyridine [Eu(*p*-ABA)₃(bipy) · H₂O]H₂O illustrates that the latter dimeric unit consists of two europium centres, each of these is coordinated to two bridged carboxyl groups, one chelating carboxyl and one monodentate carboxyl groups, one bipyridine molecule and one water molecule.⁶ In the crystal lattice of the latter complex, dimers are further linked via intermolecular O—H—O hydrogen bonds between water molecules and carboxyl oxygen atoms of the carboxyl groups. Possibly, such difference arises from differing positions of the amino substituent in the benzene ring.

IR and Raman spectra

IR and Raman studies indicate that bands present in the complex but not the free ligand at 1581

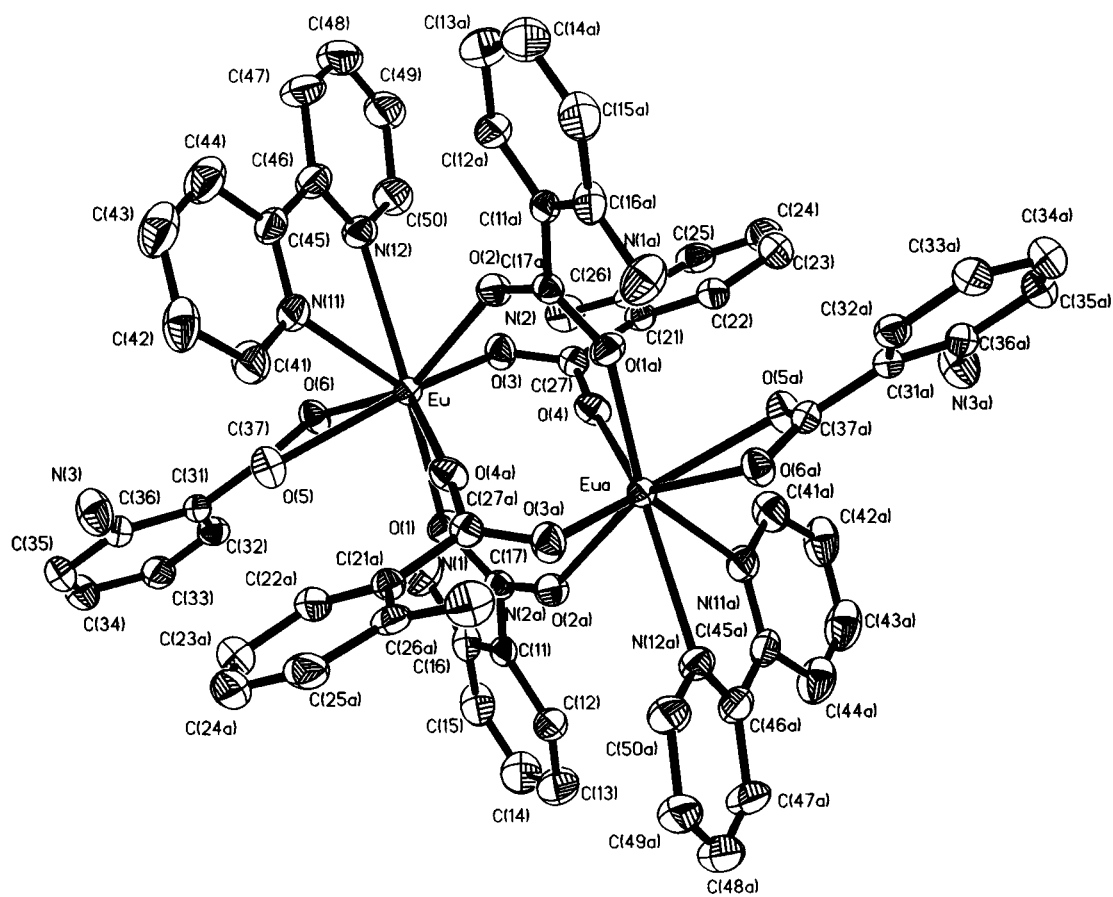


Fig. 1. The molecular structure of [Eu(*o*-ABA)₃bipy]bipy.

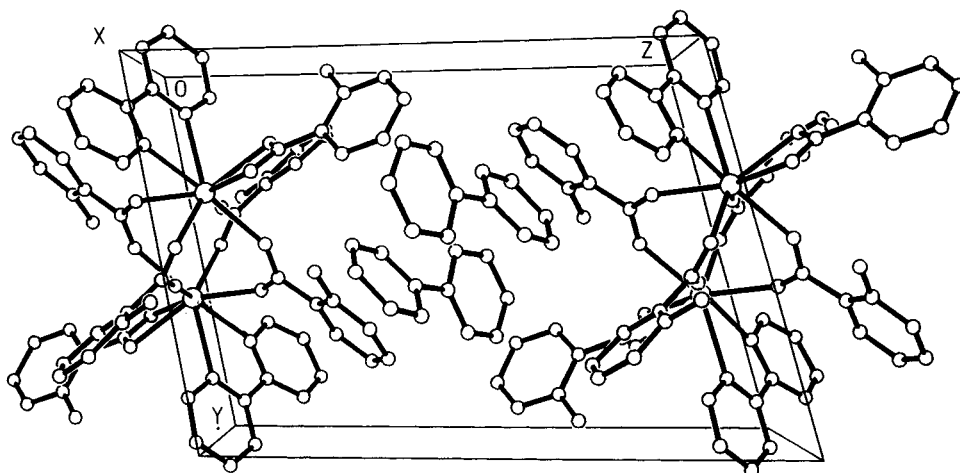


Fig. 2. Packing diagram of [Eu(*o*-ABA)₃bipy]bipy.

Table 2. Bond distances (nm)

Eu—O(1)	0.2374(3)	C(31)—C(36)	0.1419(6)
Eu—O(2)	0.2334(3)	C(31)—C(37)	0.1484(6)
Eu—O(3)	0.2398(3)	C(32)—C(33)	0.1379(6)
Eu—O(4a)	0.2330(3)	C(33)—C(34)	0.1401(7)
Eu—O(5)	0.2436(3)	C(34)—C(35)	0.1381(7)
Eu—O(6)	0.2508(3)	C(35)—C(36)	0.1404(6)
Eu—N(11)	0.2593(3)	C(41)—C(42)	0.1395(6)
Eu—N(12)	0.2658(3)	C(41)—N(11)	0.1350(6)
O(1)—C(17)	0.1268(5)	C(42)—C(43)	0.1381(6)
O(2)—C(17)	0.1259(5)	C(43)—C(44)	0.1396(8)
O(3)—C(27)	0.1251(5)	C(44)—C(45)	0.1406(7)
O(4)—C(27)	0.1270(5)	C(45)—C(46)	0.1469(7)
O(5)—C(37)	0.1265(5)	C(45)—N(11)	0.1344(6)
O(6)—C(37)	0.1263(5)	C(46)—N(12)	0.1348(6)
N(1)—C(16)	0.1385(6)	C(46)—C(47)	0.1412(7)
N(2)—C(26)	0.1378(6)	C(47)—C(48)	0.1398(8)
N(3)—C(36)	0.1379(6)	C(48)—C(49)	0.1396(9)
C(11)—C(12)	0.1406(6)	C(49)—C(50)	0.1412(8)
C(11)—C(16)	0.1404(6)	C(50)—N(12)	0.1350(6)
C(11)—C(12)	0.1495(6)	C(51)—C(52)	0.1393(8)
C(12)—C(13)	0.1400(7)	C(51)—N(21)	0.1342(7)
C(13)—C(14)	0.1384(8)	C(52)—C(53)	0.1385(8)
C(14)—C(15)	0.1385(8)	C(53)—C(54)	0.1392(7)
C(15)—C(16)	0.1418(6)	C(54)—C(55)	0.1397(6)
C(21)—C(22)	0.1400(7)	C(55)—C(56)	0.1495(6)
C(21)—C(26)	0.1413(6)	C(55)—N(21)	0.1336(6)
C(21)—C(27)	0.1482(5)	C(56)—C(57)	0.1383(6)
C(22)—C(23)	0.1394(7)	C(56)—N(22)	0.1343(6)
C(23)—C(24)	0.1407(8)	C(57)—C(58)	0.1405(7)
C(24)—C(25)	0.1374(8)	C(58)—C(59)	0.1383(8)
C(25)—C(26)	0.1409(7)	C(59)—C(60)	0.1379(8)
C(31)—C(32)	0.1397(6)	C(60)—N(22)	0.1347(6)

(IR), 1571 and 1565 cm^{-1} (Raman) and 1418 (IR), 1405 and 1399 cm^{-1} (Raman), assigned, respectively, to asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of the carboxyl group. This clearly shows that hydrogen was displaced by europium ion from the carboxyl group. An analysis of shapes of the $\nu_{\text{s}}(\text{COO})$ bands indicates that the europium ion is bound to the carboxyl group in different modes. This result agrees with X-ray analysis. Raman bands at 1571 and 1399 cm^{-1} are assigned, respectively, to ν_{as} and $\nu_{\text{s}}(\text{COO})$ stretching vibrations for the bridging mode, while bands at 1565 and 1405 cm^{-1} to ν_{as} and $\nu_{\text{s}}(\text{COO})$ for the bidentate mode. The difference between ν_{as} and $\nu_{\text{s}}(\text{COO})$ for the bridged carboxyl group is 172 cm^{-1} and that for the bidentate one is 160 cm^{-1} . The detailed data are given in Table 4.

Luminescence properties

The luminescence spectra under UV light excitation were obtained by using the 337.1 nm line of

a N_2 laser at 77 K. Figure 3 shows UV light excited luminescence spectra of the $[\text{Eu}(\text{o-ABA})_3\text{bipy}]\text{bipy}$ complex. The luminescence spectrum observed in the 578–582 nm region shown in Fig. 3(a) is usually attributed to the transition between 5D_0 and 7F_0 states of Eu^{3+} in the complex. Since only one luminescence band should be observed from Eu^{3+} in one state, it is obvious that one site is occupied by Eu^{3+} in $[\text{Eu}(\text{o-ABA})_3\text{bipy}]\text{bipy}$. This differs from the europium *p*-methylbenzoate complex with 2,2'-bipyridine which involved Eu^{3+} in two sites. However, a symmetric centre occurs in the crystal structure of this dinuclear complex.⁵ It is not surprising that the luminescence spectra reflect the properties of the excited state and not of the ground state. Furthermore, the relative intensity of the luminescence bands arising from $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of the title complex indicates that the bands of $^5D_0 \rightarrow ^7F_2$ transition predominate. This observation illustrates no inversion centre is occupied by Eu^{3+} in the complex. Figures 3(b) and (c) show that the transitions to the 7F_1 and 7F_2 levels

Table 3. Bond angles (°)

O(1)—Eu—O(2)	129.9(1)	C(11)—C(16)—C(15)	118.3(5)
O(1)—Eu—O(3)	78.5(2)	O(1)—C(17)—O(2a)	124.6(4)
O(1)—Eu—O(4a)	76.9(1)	O(1)—C(17)—C(11)	117.9(4)
O(1)—Eu—O(5)	77.3(2)	O(2)—C(17a)—C(11a)	117.5(4)
O(1)—Eu—O(6)	72.50(9)	C(22)—C(21)—C(26)	120.7(4)
O(1)—Eu—N(11)	142.2(2)	C(22)—C(21)—C(27)	117.4(4)
O(1)—Eu—N(12)	145.1(2)	C(26)—C(21)—C(27)	121.9(4)
O(2)—Eu—O(3)	82.9(2)	C(21)—C(22)—C(23)	120.9(4)
O(2)—Eu—O(4a)	76.8(1)	C(22)—C(23)—C(24)	117.9(4)
O(2)—Eu—O(5)	143.1(1)	C(23)—C(24)—C(25)	122.0(5)
O(2)—Eu—O(6)	148.22(9)	C(24)—C(25)—C(26)	120.5(5)
O(2)—Eu—N(11)	75.8(2)	N(2)—C(26)—C(21)	123.6(4)
O(2)—Eu—N(12)	70.8(2)	N(2)—C(26)—C(25)	118.5(5)
O(3)—Eu—O(4a)	124.9(2)	C(21)—C(26)—C(25)	117.9(4)
O(3)—Eu—O(5)	131.7(1)	O(3)—C(27)—C(4)	122.1(4)
O(3)—Eu—O(6)	80.5(1)	O(3)—C(27)—C(21)	119.2(4)
O(3)—Eu—N(11)	137.9(1)	O(4)—C(27)—C(21)	118.7(4)
O(3)—Eu—N(12)	76.9(2)	C(32)—C(31)—C(36)	119.5(4)
O(4a)—Eu—O(5)	89.0(1)	C(32)—C(31)—C(37)	118.7(4)
O(4a)—Eu—O(6)	134.75(9)	C(36)—C(31)—C(37)	121.8(4)
O(4a)—Eu—N(11)	85.2(1)	C(31)—C(32)—C(33)	122.3(4)
O(4a)—Eu—N(12)	138.0(2)	C(32)—C(33)—C(34)	118.0(4)
O(5)—Eu—O(6)	52.52(9)	C(33)—C(34)—C(35)	121.2(4)
O(5)—Eu—N(11)	69.2(2)	C(34)—C(35)—C(36)	121.2(4)
O(5)—Eu—N(12)	101.5(2)	N(3)—C(36)—C(31)	123.0(4)
O(6)—Eu—N(11)	99.2(2)	N(3)—C(36)—C(35)	119.3(5)
O(6)—Eu—N(12)	79.2(2)	C(31)—C(36)—C(35)	117.7(4)
N(11)—Eu—N(12)	61.9(1)	O(5)—C(37)—O(6)	120.0(4)
Eu—O(1)—C(17)	137.0(3)	O(5)—C(37)—C(31)	119.5(4)
Eu—O(2)—C(17a)	138.3(3)	O(6)—C(37)—C(31)	120.5(4)
Eu—O(3)—C(27)	106.7(2)	C(42)—C(41)—N(11)	122.7(5)
Eu—O(4a)—C(27a)	80.8(2)	C(41)—C(42)—C(43)	118.2(5)
Eu—O(5)—C(37)	95.1(2)	C(42)—C(43)—C(44)	119.9(5)
Eu—O(6)—C(37)	91.8(2)	C(43)—C(44)—C(45)	118.6(6)
C(12)—C(11)—C(16)	120.4(4)	C(44)—C(45)—C(46)	121.6(5)
C(12)—C(11)—C(17)	116.3(4)	C(44)—C(45)—N(11)	121.6(5)
C(16)—C(11)—C(17)	123.3(4)	C(46)—C(45)—N(11)	116.8(4)
C(11)—C(12)—C(13)	120.9(5)	C(45)—C(46)—C(47)	120.9(5)
C(12)—C(13)—C(14)	118.3(5)	C(45)—C(46)—N(12)	117.4(4)
C(13)—C(14)—C(15)	121.7(5)	C(47)—C(46)—N(12)	121.7(5)
C(14)—C(15)—C(16)	120.4(5)	C(46)—C(47)—C(48)	118.7(5)
N(1)—C(16)—C(11)	123.8(5)	C(47)—C(48)—C(49)	120.0(5)
N(1)—C(16)—C(15)	117.9(4)		
C(48)—C(49)—C(50)	117.9(5)	C(54)—C(55)—C(56)	119.7(4)
C(49)—C(50)—N(12)	122.5(5)	C(54)—C(55)—N(21)	123.5(4)
Eu—N(11)—C(41)	118.1(3)	C(56)—C(55)—N(21)	116.7(5)
Eu—N(11)—C(45)	122.8(4)	C(55)—C(56)—C(57)	120.3(4)
C(41)—N(11)—C(45)	119.1(4)	C(55)—C(56)—N(22)	116.3(5)
Eu—N(12)—C(46)	119.4(3)	C(57)—C(56)—N(22)	123.3(5)
Eu—N(12)—C(50)	119.9(4)	C(56)—C(57)—C(58)	117.3(6)
C(46)—N(12)—C(50)	119.5(5)	C(57)—C(58)—C(59)	119.8(5)
C(52)—C(51)—N(21)	123.0(5)	C(58)—C(59)—C(60)	118.5(5)
C(51)—C(52)—C(53)	118.9(5)	C(59)—C(60)—N(22)	122.8(5)
C(52)—C(53)—C(54)	118.7(5)	C(51)—N(21)—C(55)	117.5(5)
C(53)—C(54)—C(55)	118.2(5)	C(56)—N(22)—C(60)	118.2(5)

Table 4. IR and Raman spectral data (cm⁻¹)

IR	Raman	Assignment
3441, 3328 b		$\nu_{\text{N-H}}$
3077 m	3068 m	$\nu_{(\text{C-H})_{\text{ar}}}$
1620 vs	1615 m	$\nu_{(\text{C}=\text{C})_{\text{ar}}}$
	1593 vs	$\nu_{(\text{C}=\text{C})_{\text{ar}}}$
1581 s	1751 m	ν_{asCOO}
	1565	ν_{asCOO}
1489 s	1492 m	$\nu_{(\text{C}=\text{C})_{\text{ar}}}$
1452 s	1446 m	$\nu_{(\text{C}=\text{C})_{\text{ar}}}$
1399 s	1418 s	ν_{sCOO}
	1405 m	ν_{sCOO}
	1310 s	$\nu_{(\text{C-H})_{\text{ar}}}$
1304 m	1303 m	Φ_{CH} out-of-plane bend
1157 s	1156 w	Φ_{CH} in-plane bend
1064 m	1063 m	Ring deformation
1013 m	1012 m	Ring deformation
991 w	995 m	In-plane breathing
814 m	814 m	Φ_{CH} out-of-plane bend
666 m	670 w	Ring deformation
444 w	450 w	$\nu_{\text{Eu-N}}$
	427 w	$\nu_{\text{Eu-O}}$
406 w	410 w	$\nu_{\text{Eu-O}}$
	160 m,b	$\nu_{\text{Eu-O}}$ chelate ring deformation

vs : very strong, s : strong, m : medium, w : weak, b : broad.

Table 5. Luminescence data

E (cm ⁻¹)	λ (nm)	E_0 (cm ⁻¹)	IR	Raman (cm ⁻¹)	Assignment
17244	579.91	0			$^5D_0 \rightarrow ^7F_0$
16954	589.83	290			$^5D_0 \rightarrow ^7F_1$
16884	592.28	360			$^5D_0 \rightarrow ^7F_1$
16794	595.45	449	444	450	Vibr ^a
16761	596.62	483			$^5D_0 \rightarrow ^7F_1$
16302	613.42	942			$^5D_0 \rightarrow ^7F_2$
16260	615.01	984			$^5D_0 \rightarrow ^7F_2$
16229	616.18	1015			$^5D_0 \rightarrow ^7F_2$
16188	617.74	1056	1064	1063	Vibr
16156	618.97	1088			$^5D_0 \rightarrow ^7F_2$
16089	621.54	1155	1157	1156	Vibr
16068	622.35	1176			$^5D_0 \rightarrow ^7F_2$
15398	649.81	1855			$^5D_0 \rightarrow ^7F_3$
15359	651.08	1885			$^5D_0 \rightarrow ^7F_3$
15339	651.94	1905			$^5D_0 \rightarrow ^7F_3$
15275	654.66	1969			$^5D_0 \rightarrow ^7F_3$
14544	687.57	2700			$^5D_0 \rightarrow ^7F_4$
14458	691.66	2786			$^5D_0 \rightarrow ^7F_4$
14401	694.40	2843			$^5D_0 \rightarrow ^7F_4$
14367	696.04	2877			$^5D_0 \rightarrow ^7F_4$
14296	699.50	2948			$^5D_0 \rightarrow ^7F_4$
14267	700.92	2977			$^5D_0 \rightarrow ^7F_4$

^aVibr : vibronic translation.

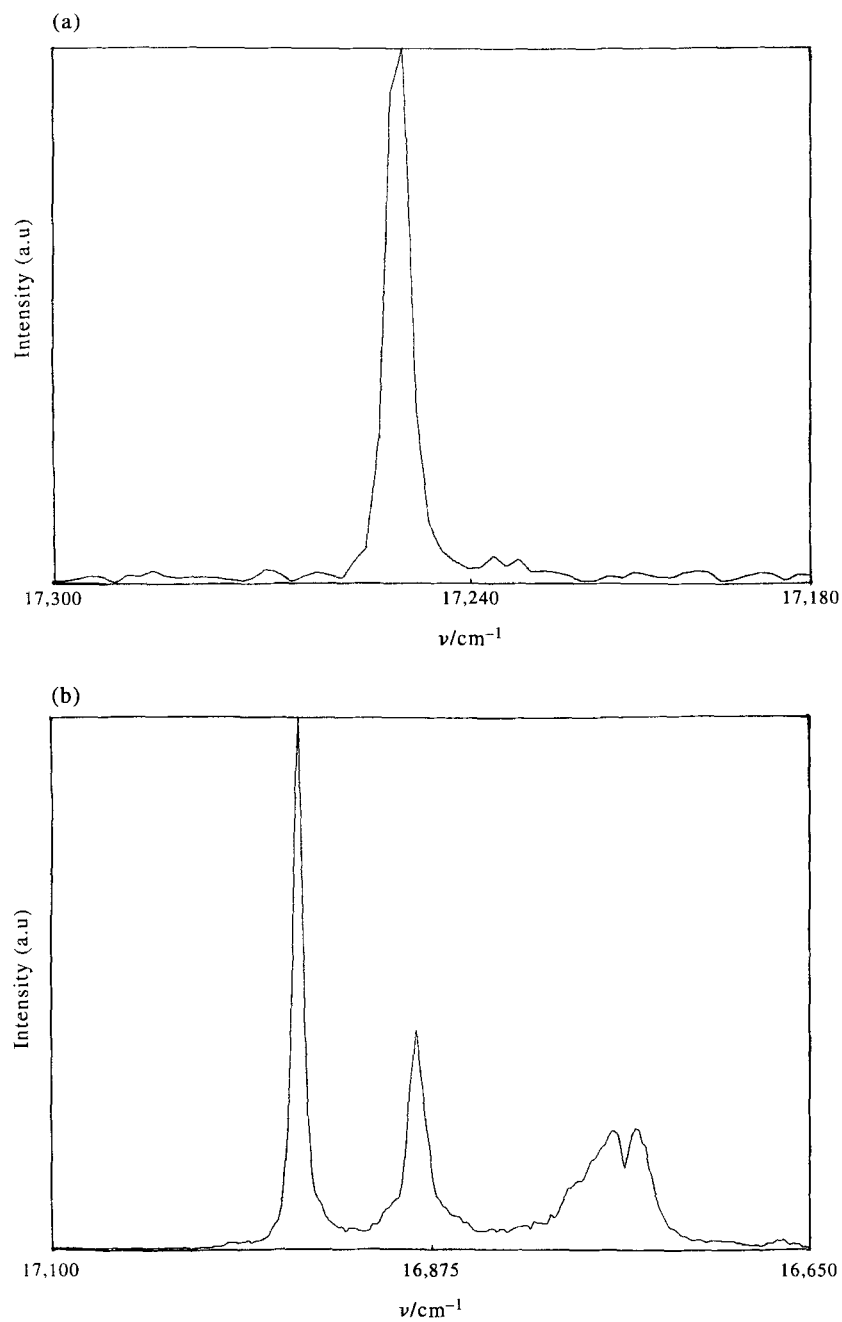


Fig. 3. Luminescence spectra of $[\text{Eu}(o\text{-ABA})_3\text{bipy}]\text{bipy}$. (a) ${}^5D_0 \rightarrow {}^7F_0$, (b) ${}^5D_0 \rightarrow {}^7F_1$, (c) ${}^5D_0 \rightarrow {}^7F_2$ and (d) ${}^5D_0 \rightarrow {}^7F_4$ transitions. Exc = 337.1 nm, 77 K.

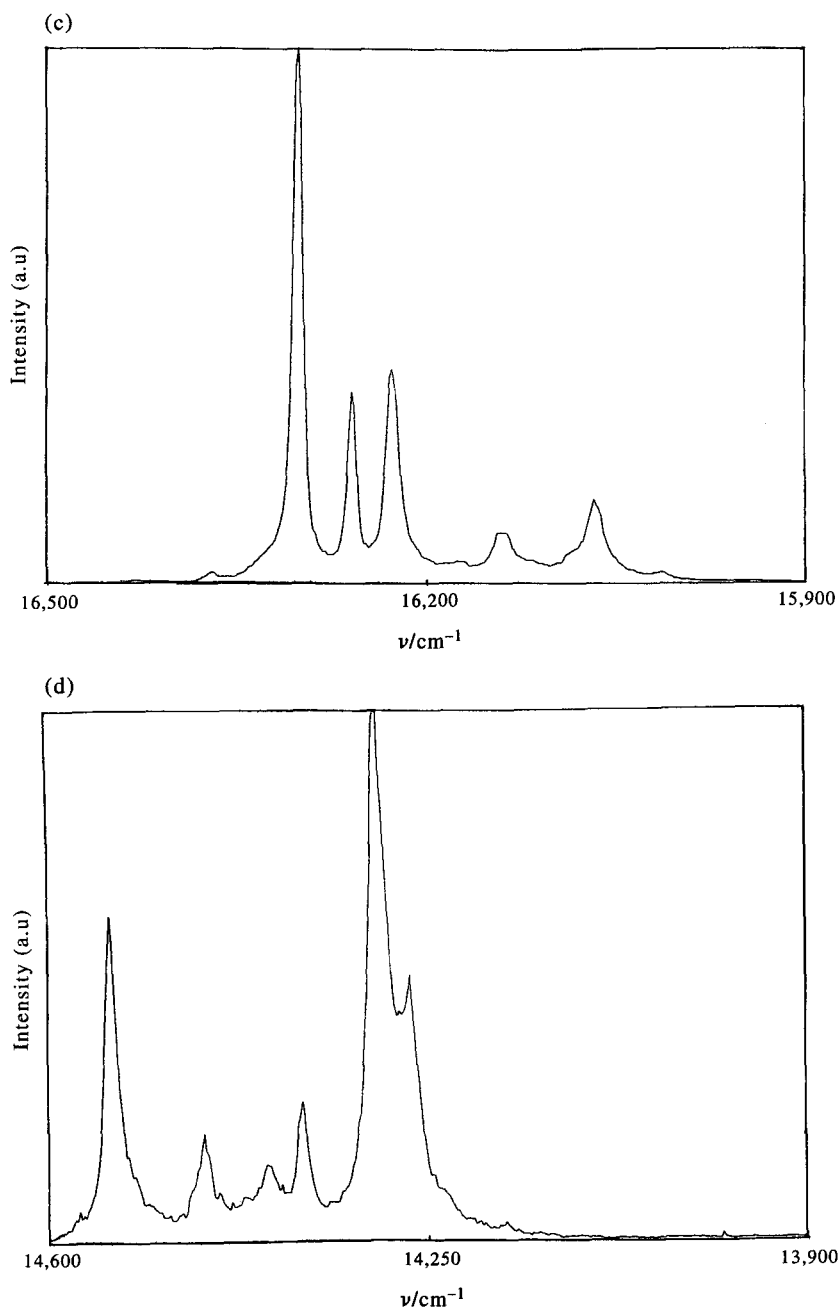


Fig. 3. (c) and (d).

comprise three and five main bands, respectively. The bands originated from the 7F_3 level are weak and those from the 7F_4 level are overlapped. Therefore, the symmetry of the Eu^{III} site in the complex is C_1 , C_s and C_2 .⁸ Probably, C_1 symmetry is reasonable as the crystal crystallizes in triclinic with $P\bar{1}$ space group. The detailed data is given in Table 5.

Acknowledgements—The project was supported by

climbing program—A fundamental Research Key Project and NNSFC grant.

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