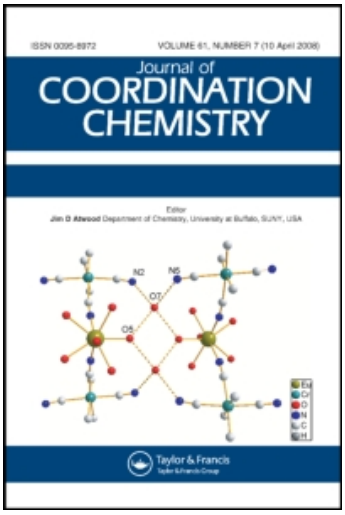

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Molecular and Crystal Structure of 1,1'-Dimethyl-3,3'-Biisoquinoline-N,N' -Dioxide and Its 2:1 Complex with Europium Trichloride

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To cite this Article Lipkowski, Janusz , Suwińska, Kinga and Andreetti, Giovanni D.(1990) 'Molecular and Crystal Structure of 1,1'-Dimethyl-3,3'-Biisoquinoline-N,N' -Dioxide and Its 2:1 Complex with Europium Trichloride', Journal of Coordination Chemistry, 22: 2, 83 — 98
To link to this Article: DOI: 10.1080/00958979009410031
URL: http://dx.doi.org/10.1080/00958979009410031

J. Coord. Chem. 1990, Vol. 22. pp. 83–98
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MOLECULAR AND CRYSTAL STRUCTURE OF 1,1′-DIMETHYL-3,3′-BIISOQUINOLINE-*N*,*N*′-DIOXIDE AND ITS 2:1 COMPLEX WITH EUROPIUM TRICHLORIDE

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(Received February 22, 1990)

The structures of 1,1′-dimethyl-biisoquinoline-*N*,*N*′-dioxide (**1**) and of its 2:1 coordination complex with europium trichloride (**2**) have been determined by single-crystal diffractometry. The complex has a sevenfold coordination for Eu^{3+} *via* three Cl and four O donor atoms. The coordination polyhedron is a distorted pentagonal bipyramid with four oxygens and one chloride in the equatorial plane and two axial chloride ligands. Packing is of a van der Waals type and includes co-crystallized solvent molecules. Crystal data: **1**: $P2_12_12$, $a = 14.032(4)$, $b = 10.605(4)$, $c = 5.242(1)$ Å, $Z = 2$; **2**: $P2_1/c$, $a = 12.829(10)$, $b = 17.616(5)$, $c = 43.863(17)$ Å, $\beta = 91.34(4)°$, $Z = 8$.

Keywords: Europium(III), biisoquinoline, complex, X-ray structure

INTRODUCTION

The coordination complexes formed by lanthanide cations with *N*-oxide type ligands have recently been found to display strong luminescence[1] and are thus of interest both as new luminescent materials and as potential labels for time-resolved photoimmunoassays.[2–5]

The present study is aimed primarily at the determination of the molecular structure of the Eu^{3+} complex with 1,1′-dimethyl-biisoquinoline-*N*,*N*′-dioxide; the compound displays an unexpectedly high efficiency of UV/VIS light conversion (as high as 25% quantum yield[1]).

In this paper we report X-ray structural studies of two crystalline compounds: 1,1′-dimethyl-biisoquinoline-*N*,*N*′-dioxide (**1**) and the coordination complex of **1** with europium trichloride (**2**); the latter crystallizes in a complex solvated form.

EXPERIMENTAL

The compounds studied were synthesized as described elsewhere.[1] The crystals used for X-ray diffraction were obtained from solutions in ethyl acetate (**1**) and acetonitrile (**2**). The crystals of **2** are extremely unstable in the open air. In order to avoid

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crystal deterioration during data collection the single crystal chosen for the X-ray study was placed in a thin-walled glass capillary with some mother solution. This enabled rather complete data collection, although after long exposure to X-rays a significant decay of diffracted intensities was observed, as measured by three standard reflections. Crystal data and details concerning data collection and structure determination for **1** and **2** are listed in Table I.

TABLE I
Crystallographic data for the complexes **1** and **2**.

	1	**2**
Molecular formula	$C_{20}H_{16}N_2O_2$	$(C_{20}H_{16}N_2O_2)_2 \cdot EuCl_3 \cdot$solvent
Crystal dimensions (mm)	0.20 × 0.30 × 0.30	0.15 × 0.20 × 0.30
Space group	orthorhombic, $P2_12_12$	monoclinic, $P2_1/c$
a (Å)	14.032(4)	12.829(10)
b (Å)	10.605(4)	17.616(5)
c (Å)	5.242(1)	43.863(7)
β (°)		91.34(4)
V (Å^3)	780.1(7)	9891(12)
λ (Å)	Mo (0.71073)	Cu (1.54178)
d_{calc} (g/cm^3)	1.347	1.414 (see text)
μ (cm^{-1})	0.823	98.62
Z	2	8
$F(000)$	332	3784
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.70	0.56
h, k, l *range*	$0 \leqslant h \leqslant 19, 0 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 7$	$0 \leqslant h \leqslant 12, 0 \leqslant k \leqslant 19, -49 \leqslant l \leqslant 49$
No. of reflections measured	1386	17016
No. of unique reflections	1386	15751
R_{int}		0.052
No. of observed reflections	897	7893
Structure solution	direct methods (MULTAN11/82)	Patterson method
Structure refinement (on F)	full-matrix	block-diagonal full-matrix
Absorption	ignored	DIFABS[11]
Weighting scheme	$1/\sigma^2(F)$	$3.1457/(\sigma^2(F) + 0.0003F^2)$
H-atoms	refined x, y, z, U_{iso}	'riding', $U_{iso} = 0.10$ Å^2
Av. shift to e.s.d. ratio	0.02	0.07
Max. and min. Δδ (e/Å^3)	0.20, −0.16	0.93, −0.55
R, R_w	0.035, 0.031	0.072, 0.067

The structure of **1** was solved and refined with the SDP system of programs.[12] The structure of **2** was solved by the Patterson method. The positions of two symmetrically independent Eu^{3+} cations were thus determined. A few cycles of subsequent Fourier maps (SHELXS[7]) revealed most of the non-hydrogen atoms for **2**. Consecutive difference Fourier map calculations (CRYSRULER[8]) revealed the complete structures of the two independent molecules of the Eu^{3+} complex. Positions of the solvent molecules were found at different stages of the refinement procedure.

RESULTS AND DISCUSSION

Final atomic coordinates of non-hydrogen atoms, bond lengths and angles are listed in Tables II to V. Lists of hydrogen positions, anisotropic thermal parameters and

observed and calculated structure factors have been deposited with the Editor and are available upon request.

TABLE II

Fractional atomic coordinates [$\times 10^4$] and *B*eq with e.s.d.s (in parentheses) for non-hydrogen atoms for **1**.

Atom	*x/a*	*y/b*	*z/c*	*B*eq
O	47(1)	1523(1)	5812(3)	4.00(3)
N	721(1)	1138(1)	4309(3)	2.92(3)
C(1)	500(1)	218(2)	2489(4)	2.82(4)
C(2)	1146(1)	−166(2)	778(4)	2.94(4)
C(3)	2090(1)	305(2)	848(4)	2.71(4)
C(4)	2321(1)	1200(2)	2749(4)	2.80(4)
C(5)	1611(1)	1630(2)	4462(4)	2.86(4)
C(6)	2783(1)	−80(2)	−926(4)	3.55(4)
C(7)	3686(1)	397(2)	−824(5)	4.16(5)
C(8)	3927(1)	1274(2)	1053(5)	4.32(5)
C(9)	3272(1)	1669(2)	2822(5)	3.64(5)
C(m)	1738(2)	2630(2)	6413(5)	3.91(5)

TABLE III

Fractional atomic coordinates [$\times 10^4$] and *B*eq with e.s.d.s (in parentheses) for non-hydrogen atoms for **2**.

Atom	*x/a*	*y/b*	*z/c*	*B*eq
Eu(1)	3095(1)	2824(0)	908(0)	3.78(2)
Cl(11)	1562(3)	3829(2)	964(1)	5.90(11)
Cl(12)	4438(3)	1676(2)	848(1)	5.49(10)
Cl(13)	4677(3)	3806(2)	1058(1)	8.75(15)
O(11)	3169(5)	2779(4)	1448(2)	3.99(24)
N(11)	3312(8)	2143(5)	1607(2)	3.36(31)
C(111)	2430(9)	1721(7)	1692(2)	3.33(35)
C(112)	2572(11)	1074(7)	1862(2)	4.12(40)
C(113)	3537(11)	802(7)	1947(3)	4.10(42)
C(114)	4431(11)	1222(6)	1864(3)	3.78(41)
C(115)	4282(10)	1917(6)	1695(2)	3.36(34)
C(116)	3697(14)	98(8)	2094(3)	5.91(52)
C(117)	4650(15)	−162(10)	2153(3)	7.49(66)
C(118)	5487(14)	260(9)	2088(3)	7.33(62)
C(119)	5428(10)	940(8)	1939(3)	5.15(48)
C(11M)	5153(9)	2414(7)	1604(3)	4.62(40)
O(12)	1888(5)	1880(4)	1097(2)	3.82(23)
N(12)	1145(8)	2081(5)	1290(2)	3.38(30)
C(121)	1422(9)	2049(6)	1597(3)	3.26(34)
C(122)	689(11)	2269(6)	1805(3)	4.68(40)
C(123)	−298(10)	2518(7)	1708(3)	4.75(44)
C(124)	−544(10)	2544(7)	1392(3)	4.66(45)
C(125)	203(10)	2304(7)	1184(3)	4.58(44)
C(126)	−1067(13)	2781(8)	1922(3)	7.06(50)
C(127)	−2018(12)	3048(9)	1806(5)	7.04(62)
C(128)	−2247(13)	3066(9)	1509(5)	7.52(67)
C(129)	−1517(11)	2804(8)	1283(4)	6.22(51)
C(12M)	17(9)	2269(7)	851(3)	5.02(38)

TABLE III (*cont.*)

Atom	*x/a*	*y/b*	*z/c*	*B*eq
O(13)	3535(7)	3420(5)	452(2)	6.00(33)
N(13)	2876(10)	3650(9)	241(3)	6.49(52)
C(131)	2496(12)	3165(11)	13(4)	5.97(55)
C(132)	1864(13)	3400(12)	−210(4)	7.43(68)
C(133)	1517(14)	4146(15)	−217(5)	8.24(72)
C(134)	1875(15)	4684(14)	1(6)	8.23(81)
C(135)	2594(14)	4397(14)	241(4)	6.75(62)
C(136)	794(20)	4361(18)	−454(6)	13.29(124)
C(137)	560(29)	5145(21)	−443(8)	15.44(188)
C(138)	842(25)	5680(18)	−249(7)	14.36(136)
C(139)	1547(15)	5467(13)	0(5)	10.46(86)
C(13M)	3018(13)	4896(9)	460(4)	8.46(71)
O(14)	2152(6)	2237(5)	483(2)	4.94(25)
N(14)	2615(8)	1930(7)	260(2)	4.93(34)
C(141)	2899(10)	2406(10)	26(3)	5.68(50)
C(142)	3447(12)	2080(11)	−228(3)	8.28(61)
C(143)	3691(13)	1289(12)	−234(4)	8.17(63)
C(144)	3334(11)	832(11)	0(3)	6.95(55)
C(145)	2804(11)	1208(10)	249(3)	5.54(51)
C(146)	4214(15)	1048(13)	−487(4)	10.79(88)
C(147)	4399(14)	271(16)	−483(4)	11.27(108)
C(148)	4106(14)	−219(12)	−261(4)	9.99(79)
C(149)	3556(13)	44(10)	−21(4)	8.22(64)
C(14M)	2398(11)	751(8)	491(3)	6.59(54)
Eu(2)	156(1)	3652(0)	2894(0)	3.24(02)
Cl(21)	−1724(2)	3653(2)	2624(1)	4.99(11)
Cl(22)	2043(2)	3826(2)	3154(1)	5.54(10)
Cl(23)	125(3)	2134(2)	2958(1)	7.49(13)
O(21)	984(5)	3154(4)	2450(1)	3.30(21)
N(21)	1908(8)	3407(5)	2353(2)	3.59(29)
C(211)	1893(9)	4036(6)	2150(3)	3.49(37)
C(212)	2811(10)	4282(6)	2046(3)	4.29(42)
C(213)	3795(10)	3966(7)	2134(3)	4.28(40)
C(214)	3786(9)	3337(7)	2328(3)	3.61(36)
C(215)	2804(9)	3041(6)	2436(3)	3.73(38)
C(216)	4758(11)	4244(7)	2041(3)	5.74(47)
C(217)	5688(11)	3930(8)	2138(3)	5.63(53)
C(218)	5641(10)	3332(9)	2324(3)	5.48(50)
C(219)	4742(9)	2989(7)	2421(2)	3.96(37)
C(21M)	2709(9)	2357(6)	2630(3)	4.58(39)
O(22)	582(6)	4675(4)	2556(2)	3.88(25)
N(22)	266(7)	4693(5)	2270(2)	3.57(28)
C(221)	873(9)	4329(6)	2050(3)	3.34(35)
C(222)	612(10)	4332(6)	1759(3)	3.78(34)
C(223)	−344(10)	4665(7)	1659(3)	4.49(42)
C(224)	−970(10)	5012(7)	1888(3)	4.70(43)
C(225)	−621(10)	5044(6)	2190(3)	3.39(36)
C(226)	−689(12)	4641(8)	1352(3)	6.75(54)
C(227)	−1576(14)	4925(11)	1253(4)	9.51(69)
C(228)	−2211(14)	5279(11)	1479(5)	10.60(74)

TABLE III (*cont.*)

Atom	*x/a*	*y/b*	*z/c*	*B*eq
C(229)	−1953(12)	5332(9)	1797(3)	7.72(55)
C(22M)	−1127(10)	5472(6)	2431(3)	4.96(45)
O(23)	−662(6)	3452(4)	3373(2)	4.13(26)
N(23)	−1580(8)	3759(5)	3449(2)	3.82(29)
C(231)	−1561(10)	4471(6)	3592(2)	3.47(36)
C(232)	−2436(10)	4812(6)	3686(2)	3.83(36)
C(233)	−3406(10)	4460(7)	3635(3)	3.88(40)
C(234)	−3436(10)	3738(8)	3495(3)	4.42(42)
C(235)	−2497(10)	3368(8)	3407(3)	4.60(44)
C(236)	−4327(10)	4828(8)	3718(3)	5.11(47)
C(237)	−5230(15)	4492(9)	3664(4)	7.70(66)
C(238)	−5299(10)	3806(11)	3529(4)	7.69(66)
C(239)	−4427(11)	3384(8)	3436(3)	5.98(48)
C(23M)	−2422(10)	2603(6)	3267(3)	5.97(47)
O(24)	−305(6)	4866(4)	3129(2)	3.95(24)
N(24)	65(8)	5040(5)	3402(2)	3.74(33)
C(241)	−515(10)	4801(6)	3657(3)	3.98(39)
C(242)	−170(11)	4925(7)	3941(3)	5.19(46)
C(243)	773(12)	5303(8)	3989(3)	5.63(48)
C(244)	1324(11)	5551(7)	3747(3)	4.54(42)
C(245)	943(10)	5433(6)	3456(3)	4.04(41)
C(246)	1200(14)	5447(9)	4298(4)	7.68(62)
C(247)	2118(15)	5843(10)	4341(5)	8.95(72)
C(248)	2655(12)	6086(9)	4079(5)	8.01(70)
C(249)	2301(13)	5949(8)	3785(4)	7.16(60)
C(24M)	1429(10)	5698(7)	3158(3)	5.76(48)
N(1A)	4054(16)	6348(10)	2201(4)	24.46(99)
C(1A)	3147(19)	6324(11)	2298(5)	19.21(100)
C(2A)	2124(16)	6298(10)	2397(4)	18.60(93)
N(1C)	7414(22)	2802(15)	425(7)	40.14(172)
C(1C)	6417(40)	2639(27)	231(12)	49.40(369)
C(2C)	5817(25)	2980(18)	320(8)	31.75(197)
N(1D)	5313(24)	6068(17)	307(7)	43.34(213)
C(1D)	5874(35)	5368(25)	476(11)	43.53(293)
C(2D)	6218(31)	5194(22)	681(9)	43.63(285)
N(1E)	2353(29)	8436(20)	681(9)	47.19(261)
C(1E)	3088(57)	8155(44)	493(17)	84.80(649)
C(2E)	3407(42)	7455(29)	674(13)	59.56(424)
O(1?)	302(18)	8151(13)	21(5)	42.90(138)
O(9?)	142(22)	9180(15)	110(7)	58.00(200)
O(2?)	8046(22)	8352(16)	1009(7)	55.97(193)
O(3?)	−10(23)	6812(16)	1247(7)	53.61(190)
O(4?)	1186(30)	6309(19)	1094(8)	67.13(269)
O(5?)	9190(24)	8266(16)	694(7)	57.28(204)
O(6?)	7027(27)	7020(19)	1094(8)	70.61(266)
O(7?)	4709(25)	6108(17)	1323(7)	61.16(217)
O(8?)	3106(25)	5465(17)	1342(7)	61.28(221)

TABLE IV

Bond distances with e.s.d.s (in parentheses) involving non-hydrogen atoms for **1** (Å).

O–N	1.297(2)
N–C(1)	1.399(3)
N–C(5)	1.355(2)
C(1)–C(2)	1.339(3)
C(1)–C(1′)	1.479(3)
C(2)–C(3)	1.416(2)
C(3)–C(4)	1.414(3)
C(3)–C(6)	1.407(3)
C(4)–C(5)	1.417(3)
C(4)–C(9)	1.425(3)
C(5)–C(m)	1.484(3)
C(6)–C(7)	1.367(3)
C(7)–C(8)	1.396(3)
C(8)–C(9)	1.371(3)

Bond angles with e.s.d.s (in parentheses) involving non-hydrogen atoms for **1** (degrees).

O–N–C(5)	120.97(2)
O–N–C(1)	118.16(1)
C(1)–N–C(5)	120.86(2)
N–C(1)–C(1′)	115.41(2)
N–C(1)–C(2)	121.27(2)
C(2)–C(1)–C(1′)	123.18(2)
C(1)–C(2)–C(3)	120.52(2)
C(2)–C(3)–C(6)	121.72(2)
C(2)–C(3)–C(4)	118.02(2)
C(4)–C(3)–C(6)	120.25(2)
C(3)–C(4)–C(9)	117.89(2)
C(3)–C(4)–C(5)	120.11(2)
C(5)–C(4)–C(9)	121.97(2)
N–C(5)–C(4)	119.11(2)
C(4)–C(5)–C(m)	125.62(2)
N–C(5)–C(m)	115.23(2)
C(3)–C(6)–C(7)	120.43(3)
C(6)–C(7)–C(8)	120.00(3)
C(7)–C(8)–C(9)	121.20(2)
C(4)–C(9)–C(8)	120.21(3)

Structure of 1

The structure of 1,1′-dimethyl-3,3′-biisoquinoline-*N*,*N*′-dioxide is shown in Fig. 1. The molecule has twofold axial symmetry with the c_2 axis perpendicular to the C1–C1* bond. The condensed aromatic system of 1-Methyl-isoquinoline-*N*-oxide units are planar to within 0.026 Å; the O atom deviates from the mean plane by 0.08 Å. Packing of **1** shown in Fig. 2 is consistent with van der Waals intermolecular contacts.

TABLE V

Bond distances (Å) and angles (degrees) with e.s.d.s (in parentheses) involving non-hydrogen atoms for **2**.

(a) distances

Eu(1)–Cl(11)	2.658(4)	C(141)–C(142)	1.448(20)
Eu(1)–Cl(12)	2.672(3)	C(142)–C(143)	1.428(28)
Eu(1)–Cl(13)	2.731(4)	C(143)–C(144)	1.391(24)
Eu(1)–O(11)	2.371(8)	C(143)–C(146)	1.376(25)
Eu(1)–O(12)	2.429(7)	C(144)–C(145)	1.462(20)
Eu(1)–O(13)	2.339(8)	C(144)–C(149)	1.419(26)
Eu(1)–O(14)	2.431(8)	C(145)–C(14M)	1.443(20)
O(11)–N(11)	1.332(11)	C(146)–C(147)	1.390(36)
N(11)–C(111)	1.408(15)	C(147)–C(148)	1.361(29)
N(11)–C(115)	1.351(15)	C(148)–C(149)	1.358(25)
C(111)–C(112)	1.377(16)	Eu(2)–Cl(21)	2.661(3)
C(111)–C(121)	1.464(16)	Eu(2)–Cl(22)	2.661(3)
C(112)–C(113)	1.367(19)	Eu(2)–Cl(23)	2.692(3)
C(113)–C(114)	1.416(19)	Eu(2)–O(21)	2.409(5)
C(113)–C(116)	1.412(18)	Eu(2)–O(22)	2.404(7)
C(114)–C(115)	1.442(15)	Eu(2)–O(23)	2.392(8)
C(114)–C(119)	1.399(18)	Eu(2)–O(24)	2.452(7)
C(115)–C(11M)	1.480(16)	O(21)–N(21)	1.342(11)
C(116)–C(117)	1.324(25)	N(21)–C(211)	1.424(14)
C(117)–C(118)	1.341(25)	N(21)–C(215)	1.359(15)
C(118)–C(119)	1.368(20)	C(211)–C(212)	1.340(17)
O(12)–N(12)	1.338(12)	C(211)–C(221)	1.458(16)
N(12)–C(121)	1.383(15)	C(212)–C(213)	1.423(17)
N(12)–C(125)	1.342(16)	C(213)–C(214)	1.398(17)
C(121)–C(122)	1.379(18)	C(213)–C(216)	1.395(18)
C(122)–C(123)	1.396(18)	C(214)–C(215)	1.450(16)
C(123)–C(124)	1.416(18)	C(214)–C(219)	1.418(16)
C(123)–C(126)	1.450(20)	C(215)–C(21M)	1.479(16)
C(124)–C(125)	1.402(18)	C(216)–C(217)	1.372(19)
C(124)–C(129)	1.398(19)	C(217)–C(218)	1.334(20)
C(125)–C(12M)	1.477(18)	C(218)–C(219)	1.373(17)
C(126)–C(127)	1.391(22)	O(22)–N(22)	1.310(12)
C(127)–C(128)	1.330(30)	N(22)–C(221)	1.407(15)
C(128)–C(129)	1.449(25)	N(22)–C(225)	1.334(15)
O(13)–N(13)	1.300(15)	C(221)–C(222)	1.313(18)
N(13)–C(131)	1.396(22)	C(222)–C(223)	1.419(17)
N(13)–C(135)	1.365(28)	C(223)–C(224)	1.439(18)
C(131)–C(132)	1.328(24)	C(223)–C(226)	1.405(18)
C(131)–C(141)	1.434(25)	C(224)–C(225)	1.390(18)
C(132)–C(133)	1.388(33)	C(224)–C(229)	1.429(19)
C(133)–C(134)	1.420(34)	C(225)–C(22M)	1.458(17)
C(133)–C(136)	1.427(33)	C(226)–C(227)	1.306(23)
C(134)–C(135)	1.470(29)	C(227)–C(228)	1.439(27)
C(134)–C(139)	1.441(33)	C(228)–C(229)	1.429(25)
C(135)–C(13M)	1.401(26)	O(23)–N(23)	1.343(12)
C(136)–C(137)	1.413(48)	N(23)–C(231)	1.402(13)
C(137)–C(138)	1.319(47)	N(23)–C(235)	1.371(16)
C(138)–C(139)	1.448(37)	C(231)–C(232)	1.345(17)
O(14)–N(14)	1.276(13)	C(231)–C(241)	1.481(17)
N(14)–C(141)	1.382(18)	C(232)–C(233)	1.400(17)
N(14)–C(145)	1.295(21)	C(233)–C(234)	1.415(18)

TABLE V (*cont.*)

C(233)–C(236)	1.401(18)	C(244)–C(249)	1.441(21)
C(234)–C(235)	1.425(18)	C(245)–C(24M)	1.530(18)
C(234)–C(239)	1.432(19)	C(246)–C(247)	1.376(25)
C(235)–C(23M)	1.486(17)	C(247)–C(248)	1.414(29)
C(236)–C(237)	1.315(22)	C(248)–C(249)	1.383(27)
C(237)–C(238)	1.347(25)	N(1A)–C(1A)	1.245(31)
C(238)–C(239)	1.411(20)	C(1A)–C(2A)	1.389(31)
O(24)–N(24)	1.318(12)	N(1C)–C(1C)	1.544(58)
N(24)–C(241)	1.416(16)	C(1C)–C(2C)	1.055(60)
N(24)–C(245)	1.336(15)	N(1D)–C(1D)	1.601(54)
C(241)–C(242)	1.335(18)	C(1D)–C(2D)	1.043(61)
C(242)–C(243)	1.390(20)	N(1E)–C(1E)	1.361(84)
C(243)–C(244)	1.359(19)	C(1E)–C(2E)	1.518(92)
C(243)–C(246)	1.477(22)	O(1?)–O(9?)	1.869(35)
C(244)–C(245)	1.372(18)	O(3?)–O(4?)	1.905(47)

(b) angles

O(13)–Eu(1)–O(14)	70.10(31)	N(11)–C(115)–C(114)	120.47(114)
O(12)–Eu(1)–O(14)	70.20(29)	C(114)–C(115)–C(11M)	123.41(107)
O(12)–Eu(1)–O(13)	140.03(31)	N(11)–C(115)–C(11M)	116.10(98)
O(11)–Eu(1)–O(14)	139.46(28)	C(113)–C(116)–C(117)	121.16(144)
O(11)–Eu(1)–O(13)	149.95(29)	C(116)–C(117)–C(118)	120.12(158)
O(11)–Eu(1)–O(12)	69.28(26)	C(117)–C(118)–C(119)	123.62(165)
Cl(13)–Eu(1)–O(14)	143.84(23)	C(114)–C(119)–C(118)	117.62(128)
Cl(13)–Eu(1)–O(13)	74.39(25)	Eu(1)–O(12)–N(12)	120.15(56)
Cl(13)–Eu(1)–O(12)	145.58(23)	O(12)–N(12)–C(125)	119.99(94)
Cl(13)–Eu(1)–O(11)	76.62(22)	O(12)–N(12)–C(121)	115.89(97)
Cl(12)–Eu(1)–O(14)	84.93(23)	C(121)–N(12)–C(125)	124.12(101)
Cl(12)–Eu(1)–O(13)	95.12(25)	C(111)–C(121)–N(12)	119.87(99)
Cl(12)–Eu(1)–O(12)	85.94(20)	N(12)–C(121)–C(122)	117.90(115)
Cl(12)–Eu(1)–O(11)	93.45(21)	C(111)–C(121)–C(122)	121.97(110)
Cl(12)–Eu(1)–Cl(13)	91.70(16)	C(121)–C(122)–C(123)	120.75(121)
Cl(11)–Eu(1)–O(14)	90.03(23)	C(122)–C(123)–C(126)	121.67(120)
Cl(11)–Eu(1)–O(13)	88.43(24)	C(122)–C(123)–C(124)	119.25(121)
Cl(11)–Eu(1)–O(12)	87.06(21)	C(124)–C(123)–C(126)	119.03(124)
Cl(11)–Eu(1)–O(11)	86.72(22)	C(123)–C(124)–C(129)	121.25(126)
Cl(11)–Eu(1)–Cl(13)	95.68(12)	C(123)–C(124)–C(125)	119.23(120)
Cl(11)–Eu(1)–Cl(12)	172.44(14)	C(125)–C(124)–C(129)	119.52(129)
Eu(1)–O(11)–N(11)	123.89(62)	N(12)–C(125)–C(124)	118.73(116)
O(11)–N(11)–C(115)	120.90(91)	C(124)–C(125)–C(12M)	124.05(118)
O(11)–N(11)–C(111)	118.67(90)	N(12)–C(125)–C(12M)	117.21(111)
C(111)–N(11)–C(115)	120.40(90)	C(123)–C(126)–C(127)	118.11(140)
N(11)–C(111)–C(121)	114.99(96)	C(126)–C(127)–C(128)	122.54(153)
N(11)–C(111)–C(112)	118.92(110)	C(127)–C(128)–C(129)	121.99(165)
C(112)–C(111)–C(121)	126.03(111)	C(124)–C(129)–C(128)	117.07(149)
C(111)–C(112)–C(113)	123.10(114)	Eu(1)–O(13)–N(13)	125.60(83)
C(112)–C(113)–C(116)	123.49(135)	O(13)–N(13)–C(135)	118.12(135)
C(112)–C(113)–C(114)	118.48(115)	O(13)–N(13)–C(131)	121.70(139)
C(114)–C(113)–C(116)	117.91(133)	C(131)–N(13)–C(135)	120.12(144)
C(113)–C(114)–C(119)	119.41(112)	N(13)–C(131)–C(141)	115.28(142)
C(113)–C(114)–C(115)	118.53(124)	N(13)–C(131)–C(132)	122.52(178)
C(115)–C(114)–C(119)	122.02(112)	C(132)–C(131)–C(141)	122.03(164)

TABLE V (*cont.*)

C(131)-C(132)-C(133)	119.93(180)	Cl(21)-Eu(2)-Cl(23)	91.77(13)
C(132)-C(133)-C(136)	117.93(224)	Cl(21)-Eu(2)-Cl(22)	173.26(12)
C(132)-C(133)-C(134)	121.51(196)	Cl(22)-Eu(2)-Cl(23)	94.96(15)
C(134)-C(133)-C(136)	120.55(237)	Eu(2)-O(21)-N(21)	122.86(49)
C(133)-C(134)-C(139)	123.03(206)	O(21)-N(21)-C(215)	119.98(88)
C(133)-C(134)-C(135)	116.10(212)	O(21)-N(21)-C(211)	117.24(95)
C(135)-C(134)-C(139)	120.86(205)	C(211)-N(21)-C(215)	122.70(98)
N(13)-C(135)-C(134)	119.70(195)	N(21)-C(211)-C(221)	117.51(102)
C(134)-C(135)-C(13M)	119.99(187)	N(21)-C(211)-C(212)	117.61(109)
N(13)-C(135)-C(13M)	120.27(176)	C(212)-C(211)-C(221)	124.71(109)
C(133)-C(136)-C(137)	111.84(251)	C(211)-C(212)-C(213)	123.94(113)
C(136)-C(137)-C(138)	131.67(329)	C(212)-C(213)-C(216)	124.29(116)
C(137)-C(138)-C(139)	117.20(289)	C(212)-C(213)-C(214)	117.20(116)
C(134)-C(139)-C(138)	115.60(218)	C(214)-C(213)-C(216)	118.51(118)
Eu(1)-O(14)-N(14)	122.57(73)	C(213)-C(214)-C(219)	119.78(114)
O(14)-N(14)-C(145)	122.39(104)	C(213)-C(214)-C(215)	120.25(114)
O(14)-N(14)-C(141)	116.59(115)	C(215)-C(214)-C(219)	119.98(107)
C(141)-N(14)-C(145)	121.02(112)	N(21)-C(215)-C(214)	118.17(102)
C(131)-C(141)-N(14)	119.55(133)	C(214)-C(215)-C(21M)	124.34(108)
N(14)-C(141)-C(142)	118.13(145)	N(21)-C(215)-C(21M)	117.48(104)
C(131)-C(141)-C(142)	121.42(143)	C(213)-C(216)-C(217)	122.15(123)
C(141)-C(142)-C(143)	120.90(137)	C(216)-C(217)-C(218)	117.16(133)
C(142)-C(143)-C(146)	115.49(173)	C(217)-C(218)-C(219)	125.90(134)
C(142)-C(143)-C(144)	118.30(158)	C(214)-C(219)-C(218)	116.38(112)
C(144)-C(143)-C(146)	126.08(192)	Eu(2)-O(22)-N(22)	122.72(60)
C(143)-C(144)-C(149)	116.72(143)	O(22)-N(22)-C(225)	120.32(93)
C(143)-C(144)-C(145)	117.10(160)	O(22)-N(22)-C(221)	118.94(90)
C(145)-C(144)-C(149)	126.13(135)	C(221)-N(22)-C(225)	120.73(100)
N(14)-C(145)-C(144)	124.37(139)	C(211)-C(221)-N(22)	117.37(106)
C(144)-C(145)-C(14M)	118.81(140)	N(22)-C(221)-C(222)	122.25(109)
N(14)-C(145)-C(14M)	116.69(134)	C(211)-C(221)-C(222)	119.81(114)
C(143)-C(146)-C(147)	112.25(172)	C(221)-C(222)-C(223)	120.26(120)
C(146)-C(147)-C(148)	125.90(195)	C(222)-C(223)-C(226)	122.46(121)
C(147)-C(148)-C(149)	119.44(191)	C(222)-C(223)-C(224)	116.51(117)
C(144)-C(149)-C(148)	119.53(159)	C(224)-C(223)-C(226)	121.00(123)
O(23)-Eu(2)-O(24)	69.31(26)	C(223)-C(224)-C(229)	118.04(117)
O(22)-Eu(2)-O(24)	70.39(25)	C(223)-C(224)-C(225)	120.99(119)
O(22)-Eu(2)-O(23)	139.58(26)	C(225)-C(224)-C(229)	120.97(121)
O(21)-Eu(2)-O(24)	140.61(24)	N(22)-C(225)-C(224)	118.98(111)
O(21)-Eu(2)-O(23)	150.05(23)	C(224)-C(225)-C(22M)	124.91(118)
O(21)-Eu(2)-O(22)	70.34(26)	N(22)-C(225)-C(22M)	116.05(112)
Cl(21)-Eu(2)-O(24)	87.85(21)	C(223)-C(226)-C(227)	124.16(139)
Cl(21)-Eu(2)-O(23)	88.99(24)	C(226)-C(227)-C(228)	115.73(165)
Cl(21)-Eu(2)-O(22)	86.48(22)	C(227)-C(228)-C(229)	125.46(163)
Cl(21)-Eu(2)-O(21)	92.73(16)	C(224)-C(229)-C(228)	115.60(144)
Cl(22)-Eu(2)-O(24)	86.86(21)	Eu(2)-O(23)-N(23)	124.33(63)
Cl(22)-Eu(2)-O(23)	93.04(24)	O(23)-N(23)-C(235)	120.93(95)
Cl(22)-Eu(2)-O(22)	87.81(22)	O(23)-N(23)-C(231)	117.81(99)
Cl(22)-Eu(2)-O(21)	88.71(20)	C(231)-N(23)-C(235)	121.12(103)
Cl(23)-Eu(2)-O(24)	145.15(23)	N(23)-C(231)-C(241)	116.34(98)
Cl(23)-Eu(2)-O(23)	75.84(21)	N(23)-C(231)-C(232)	122.13(106)
Cl(23)-Eu(2)-O(22)	144.38(23)	C(232)-C(231)-C(241)	121.36(97)
Cl(22)-Eu(2)-O(21)	74.22(18)	C(231)-C(232)-C(233)	119.48(103)

TABLE V (*cont.*)

C(232)–C(233)–C(236)	119.90(115)	C(231)–C(241)–C(242)	121.33(114)
C(232)–C(233)–C(234)	118.99(117)	C(241)–C(242)–C(243)	118.98(124)
C(234)–C(233)–C(236)	121.10(119)	C(242)–C(243)–C(246)	121.39(136)
C(233)–C(234)–C(239)	119.07(124)	C(242)–C(243)–C(244)	120.08(130)
C(233)–C(234)–C(235)	120.93(124)	C(244)–C(243)–C(246)	118.52(138)
C(235)–C(234)–C(239)	119.99(124)	C(243)–C(244)–C(249)	121.97(132)
N(23)–C(235)–C(234)	117.18(119)	C(243)–C(244)–C(245)	119.98(129)
C(234)–C(235)–C(23M)	126.12(120)	C(245)–C(244)–C(249)	118.04(126)
N(23)–C(235)–C(23M)	116.68(111)	N(24)–C(245)–C(244)	121.29(114)
C(233)–C(236)–C(237)	118.89(133)	C(244)–C(245)–C(24M)	127.20(118)
C(236)–C(237)–C(238)	122.26(171)	N(24)–C(245)–C(24M)	111.50(105)
C(237)–C(238)–C(239)	123.85(157)	C(243)–C(246)–C(247)	120.51(161)
C(234)–C(239)–C(238)	114.82(135)	C(246)–C(247)–C(248)	118.22(179)
Eu(2)–O(24)–N(24)	119.95(60)	C(247)–C(248)–C(249)	123.49(158)
O(24)–N(24)–C(245)	124.19(94)	C(244)–C(249)–C(248)	117.24(148)
O(24)–N(24)–C(241)	117.77(93)	N(1A)–C(1A)–C(2A)	178.24(223)
C(241)–N(24)–C(245)	118.03(99)	N(1C)–C(1C)–C(2C)	106.82(435)
C(231)–C(241)–N(24)	117.03(101)	N(1D)–C(1D)–C(2D)	143.55(455)
N(24)–C(241)–C(242)	121.44(117)	N(1E)–C(1E)–C(2E)	99.09(521)

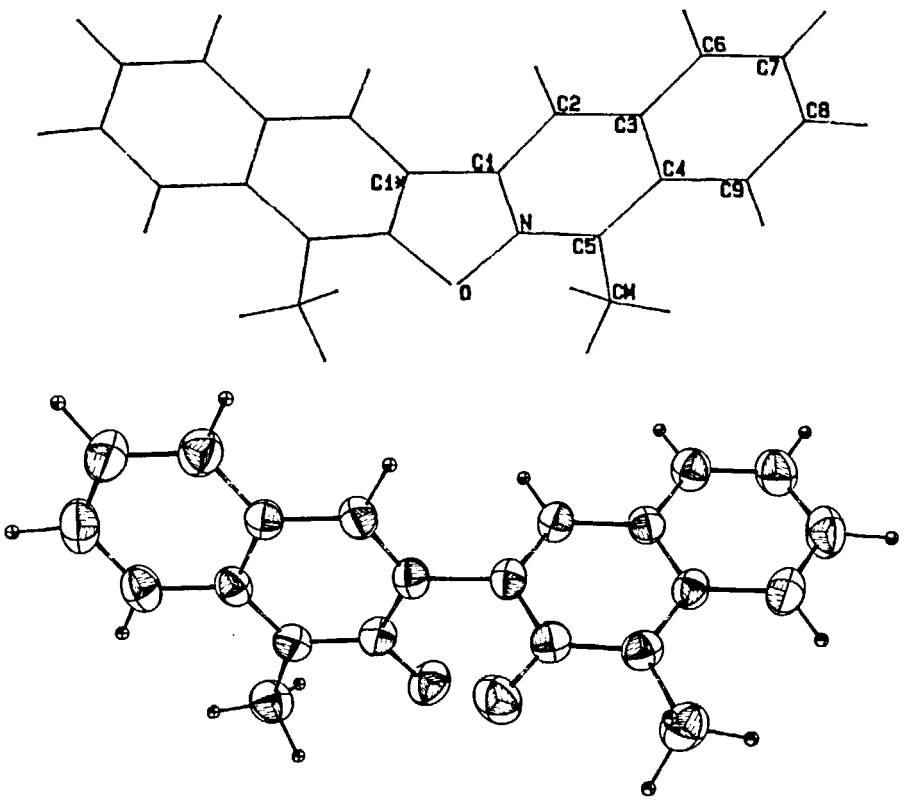

FIGURE 1 The molecule of 1; (a) numbering scheme, (b) ORTEPII[10] drawing (the thermal ellipsoids are drawn at 50% probability).

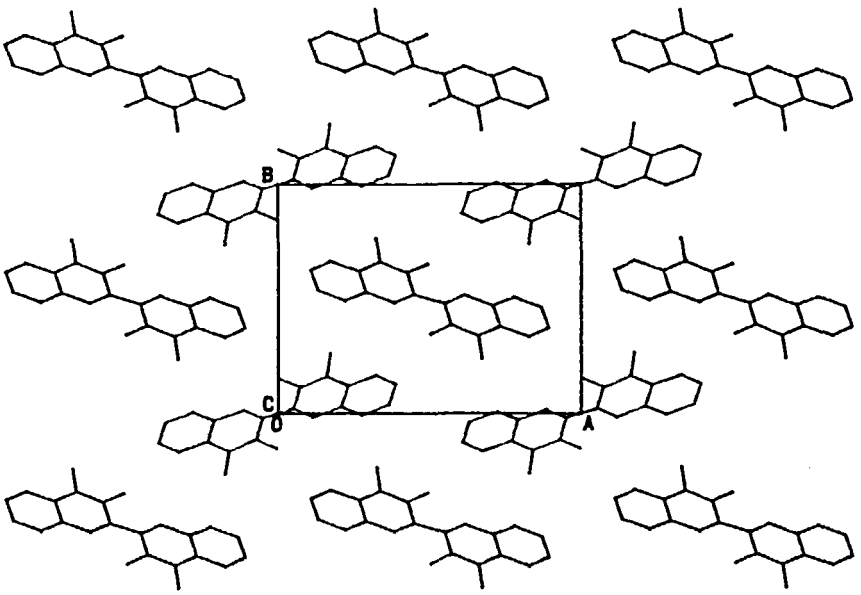

FIGURE 2 Packing of **1** in the crystal.

Structure of 2

The molecular structures of the two symmetrically independent molecules of **2** are shown in Figs. 3 and 4. The two molecules are very much alike, with minor differences in molecular geometry beyond the limits of experimental error (*c.f.* Fig. 5). The coordination polyhedra of the two molecules of the complex may be approximately described as pentagonal bipyramids. The equatorial planes of the bipyramids are defined, as illustrated in Fig. 5, by four oxygen and one chlorine atoms, the angles between coordination bonds Eu–adjacent oxygen atoms being close to 70° while the Cl–Eu–O angles within the planes are 75°. The chlorine atoms denoted Cl(11) and Cl(12) (molecule 1) or Cl(21) and Cl(22) (molecule 2) occupy the vertices of the bipyramid; the Eu–Cl axial bonds deviate by an average of 4° from the line perpendicular to the equatorial plane. The axial Eu–Cl bond lengths are slightly, but significantly, shorter than the equatorial ones (2.665(3) *vs* 2.731(4) Å in (1) and 2.661(3) *vs* 2.692(3) Å in (2)). The most significant difference in molecular structure of 1,1′-dimethyl-biisoquinoline-*N*,*N*′-dioxide in its uncoordinated form (**1**), and in the europium complex, is the N–O distance in the oxide groups and the dihedral angle between the two isoquinoline moieties. In **2**, the average N–O distance of 1.320 Å (range 1.276–1.343 Å) is longer by 0.023 Å as compared to the free ligand. The dihedral angle in **1** (103°) becomes larger in **2** by about 11° (113 and 116° in molecule 1 and 114 and 113° in molecule 2). The molecular planes of the isoquinoline moieties form angles of about 64° with the equatorial plane of the coordination polyhedron (62.6, 115.0, 65.2 and 115.9° for rings 11, 12, 13 and 14, respectively, and 65.1, 112.4, 63.6 and 112.9° for rings 21, 22, 23 and 24). The bond distances and angles within the ligand molecule are not significantly different from those in the uncomplexed molecule, with exceptions for deviations of Cm and O atoms from the molecular plane—these show minor differences which may be attributed to the influence of molecular packing in the crystal.

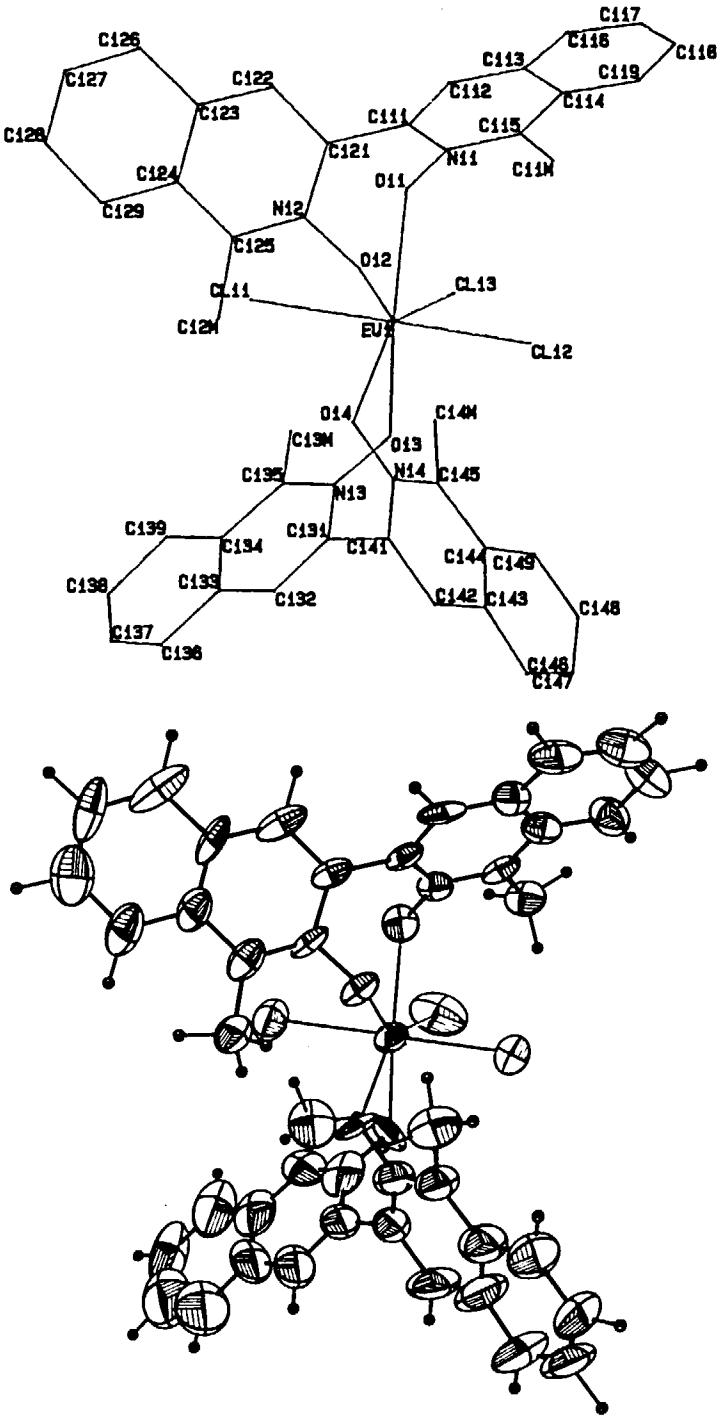

FIGURE 3 The molecule 1 of complex 2; (a) numbering scheme, (b) ORTEPII drawing[10] (the thermal ellipsoids are drawn at 50% probability).

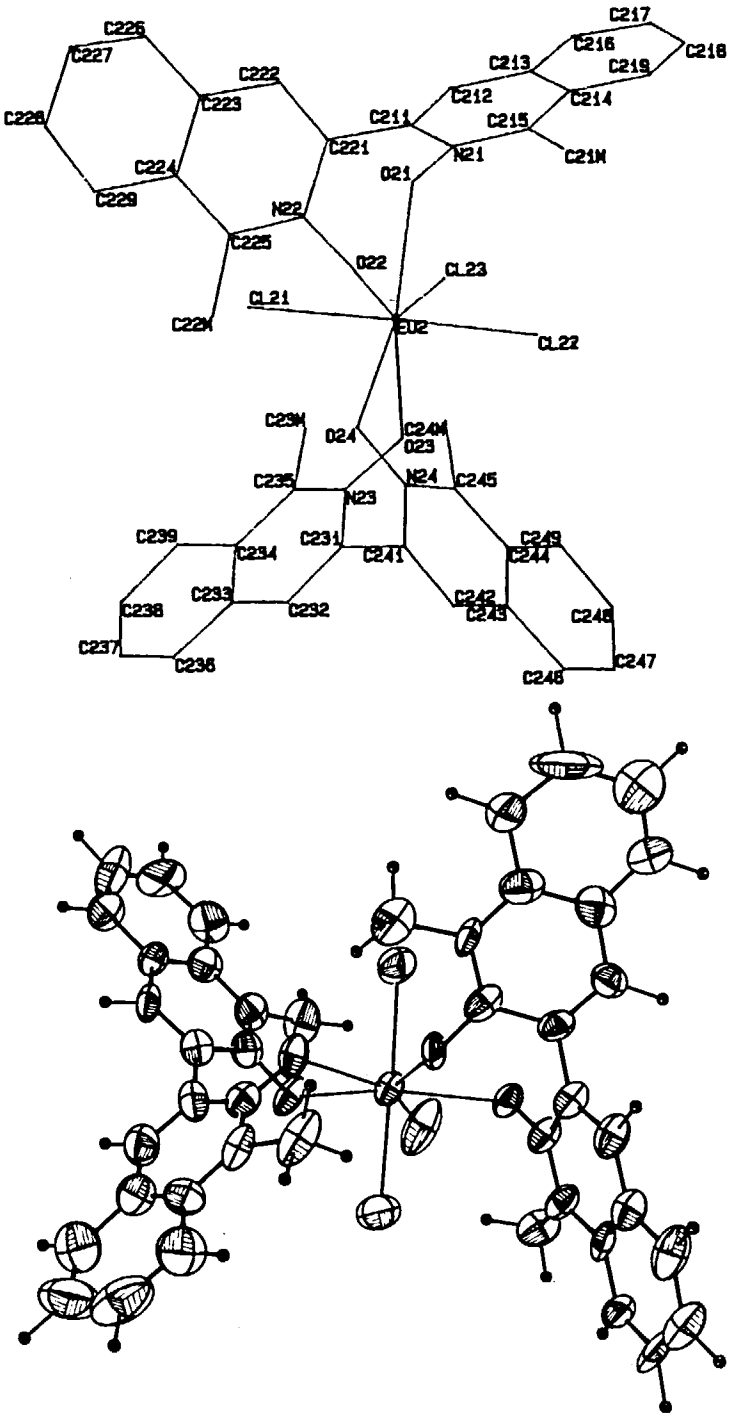

FIGURE 4 The molecule 2 of complex 2; (a) numbering scheme, (b) ORTEPII drawing[10] (the thermal ellipsoids are drawn at 50% probability).

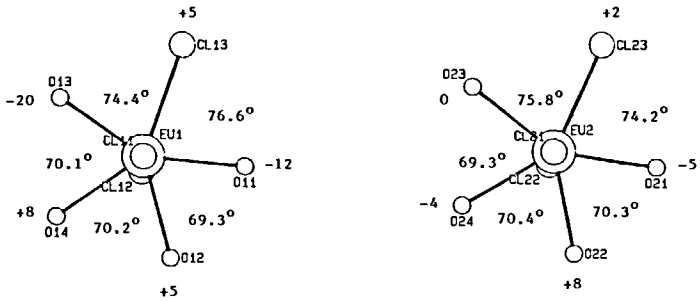

FIGURE 5 The geometry of the coordination polyhedra of the two complex molecules.

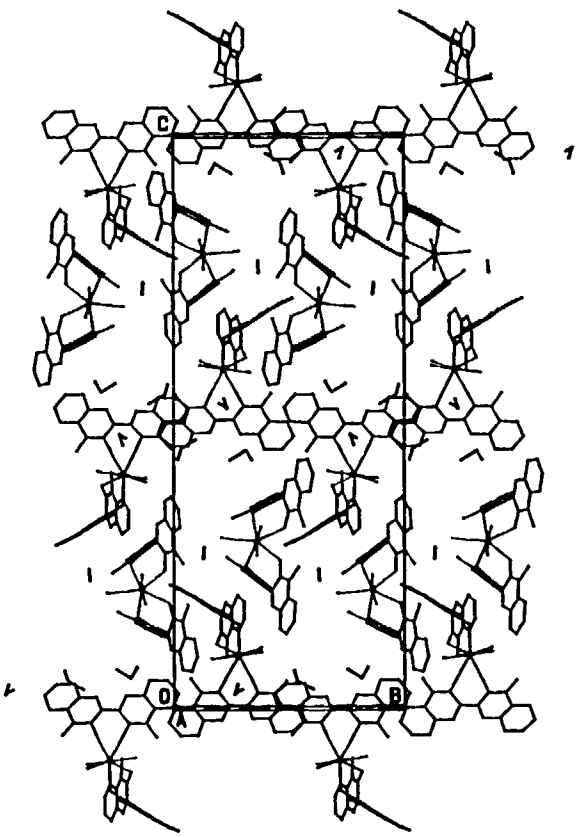

FIGURE 6 Packing of **2** in the crystal.

Molecular packing of **2** is illustrated in Fig. 6. It is worth noting the rather loose packing of the complex molecules themselves; the calculated density without taking into account the presence of the solvent is only 1.197 g cm^{-3}. Empty (*i.e.*, not occupied by Eu^{3+} complex molecules) spaces are clearly visible in Fig. 7. The solvent

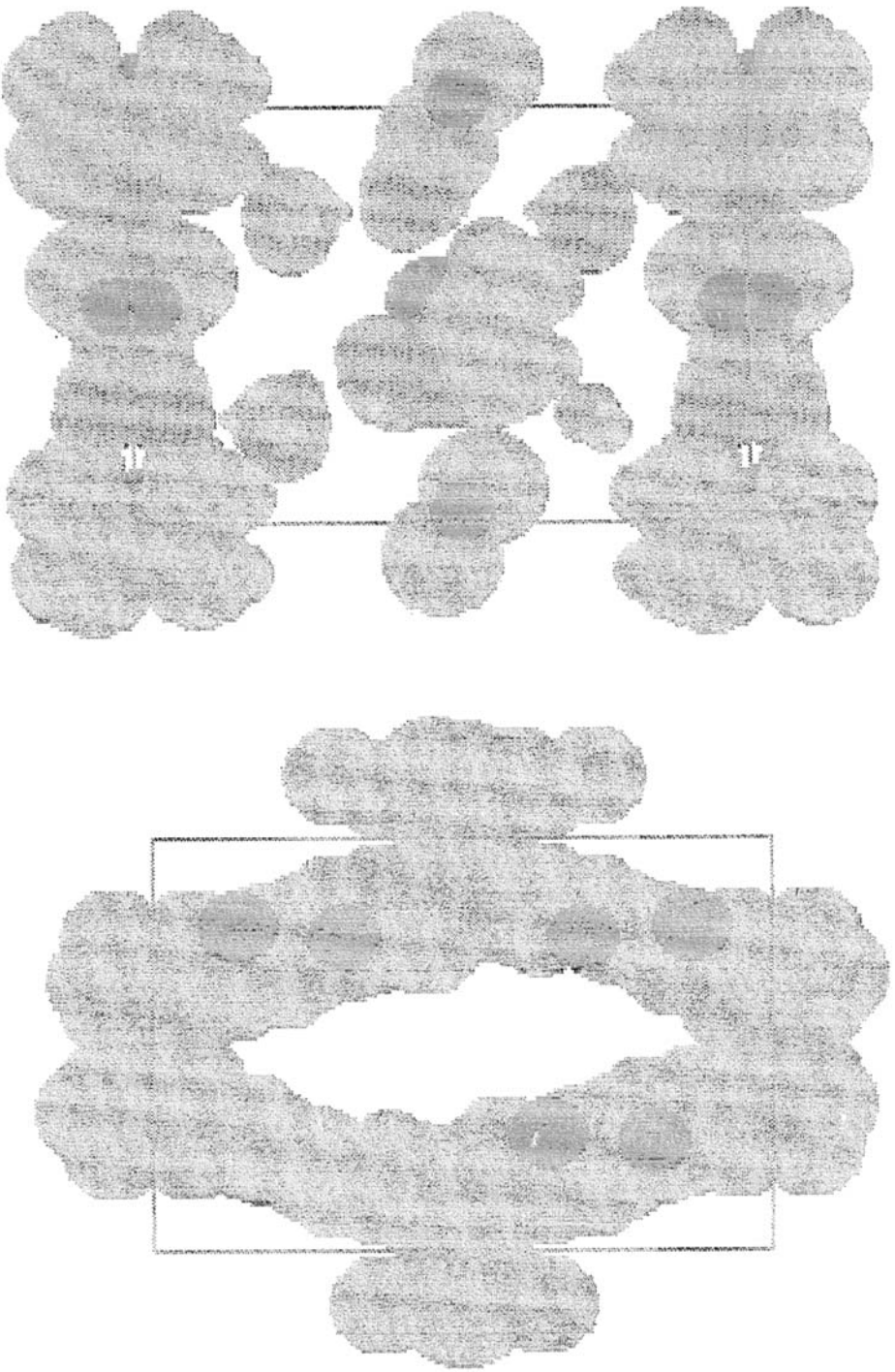

FIGURE 7 Plane sections through structure **2** parallel to (001) at (a): $c = 0.8$, and (b): $c = 1.0$.

molecules which occupy these spaces have much translational and rotational freedom—we conclude this because of the fact that the guest molecules do not 'behave' well in the refinement procedure. Just one guest–solvent molecule (denoted A) could reasonably well be identified as an acetonitrile molecule, although with rather high thermal parameters. Much effort has been expended in order to refine the guest molecules C, D and E as acetonitrile molecules (for that reason they are listed as 1N and 2C atoms each). It seems, however, that these guest molecules are in fact ethanol molecules (also used in the preparation procedure), and these are significantly disordered in the crystal. Moreover, in the final cycles of refinement, some extra residual peaks of electron density have been revealed in the 'empty' spaces of the crystal. It is assumed that these may represent possible positions of water and/or methanol molecules. Eight oxygen atoms were included (denoted On?) in the final cycles of refinement. This procedure had very little influence on the final R values and the refined isotropic thermal factors of the On? atoms are rather high. Thus little can be definitely concluded about the presence (or absence) of water (methanol?) guest molecules in the crystal structure of **2**. Calculated density with guest molecules is as follows: (i) $1.317\,g\,cm^{-3}$ with 1 acetonitrile (A) and 3 ethanol (C, D, E) guest molecules; (ii) $1.414\,g/cm^3$ with guest as above plus 8 water molecules. The extreme instability of crystals of **2** in any environment except in the presence of the mother liquor did not allow for precise density determination, such as could help in choosing between the abovementioned compositions of the co-crystallized solvent.

ACKNOWLEDGEMENTS

The study was performed within the WPR III/6 project of P.A.N.

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