Electronic Supplementary Material (ESI) for Dalton Transactions

White light emission of Eu(III) -doped Gd(III) complex with 3-sulfobenzoate and 1H-imidazo[4,5-f][1,10]-phenanthroline

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Supporting Information

Table of Contents

Experimental Section

S1. Materials and Physical measurement

$Eu(NO_3)_3\cdot 6H_2O$ and $Gd(NO_3)_3\cdot 6H_2O$ were prepared by the corresponding oxide with nitric acid. Other reagents were commercially available and were used without further purification.

Elemental analyses (C, H and N) were performed on an Elementar Vario EL analyzer. Inductively coupled plasma (ICP) spectroscopy was performed on an Agilent 7500Ce spectrometer. Infrared (IR) spectra were measured on a Bruker Tensor37 spectrophotometer using the KBr pellets technique. X-ray diffraction carried out on a PANaytical X'Pert PRO MPD diffractometer for Cu Kα radiation ($\lambda = 1.5406$ Å), with a scan speed of $2°\cdot min^{-1}$ and a step size of 0.02° in 2θ. The simulated PXRD patterns were obtained from the single-crystal X-ray diffraction data. Fluorescence spectra were recorded on an FL4500 fluorescence spectrophotometer (Japan Hitachi company) at room temperature. The lifetimes were measured at room temperature on FLS920 Steady State &Time-resolved Fluorescence Spectrometer (Edinburgh Instrument) for complex **2**. The emission quantum yields were measured at room temperature using a Quantum Yield Measurement System Fluorolog®-3 (HORIBA company) with a 450W Xe lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as sample chamber, and an analyzer R928P for signal detection. The Commission International de I'Eclairage (CIE) color coordinates were calculated on the basis of the international CIE standards[1].

S2. Synthesis of complexes **1-2**

A mixture of $Ln(NO_3)_3\cdot 6H_2O$ (0.1 mmol) (Ln = Gd and Eu), 3-sulfobenzoate (0.15 mmol), 1H-imidazo[4,5-f][1,10]-phenanthroline) (0.1 mmol), H_2O (10 mL), and an aqueous solution of NaOH (2 mol/L, 0.10 mL) was sealed in a Teflon-lined reactor and heated at 140 °C for 3 days. After slow cooling to room temperature, block crystals of the complexes were obtained. Yield: 47% for **1** and 52% for **2** based on the Ln(III). For **1**: Anal. Calc. for $C_{20}H_{17}N_4O_8SGd$: C, 38.09; N, 8.88; H, 2.72%. Found: C, 38.32; N, 8.96; H, 2.94%. Selected IR (KBr pellet, cm^{-1}): 3336(s), 2901(w), 1592(m), 1578(s), 1536(vs), 1428(vs), 1392(vs), 1354(vs), 1307(w), 1184(s), 1078(m), 1038(m), 997(m), 883(w), 838(w), 763(m), 671(m), 636(w), 417(w). For **2**: Anal. Calc. for $C_{20}H_{17}N_4O_8SEu$: C,38.41; N, 8.96; H, 2.74%. Found: C, 38.74; N, 9.23; H, 2.86%. Selected IR (KBr pellet, cm^{-1}): 3337(s), 2872(w), 1592(m), 1577(s), 1536(vs), 1428(vs), 1392(vs), 1354(vs), 1307(w), 1184(s), 1078(m), 1038(m), 998(m), 881(w), 838(w), 734(m), 670(m), 636(w), 412(w).

S3. X-ray crystal structure determination

The X-ray single crystal data collections for the two complexes were performed on a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Semiempirical absorption correction was applied on the complex using the SADABS program. The structure was solved by direct methods and refined by full matrix least squares method on F^2 using SHELXS 97 and SHELXL 97 programs. [2, 3] All non-hydrogen atoms in the complexes were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. A summary of the crystallographic data and details of the structure refinements are listed in Table S3. Selected bond distances and bond angles are listed in Table S4.

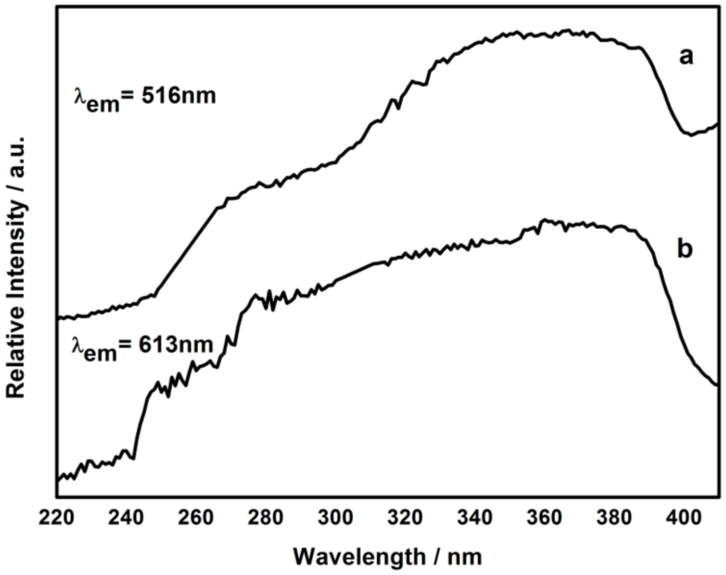


Figure S1. Excitation spectra of complexes **1** (a) and **2** (b) in the solid state at room temperature.

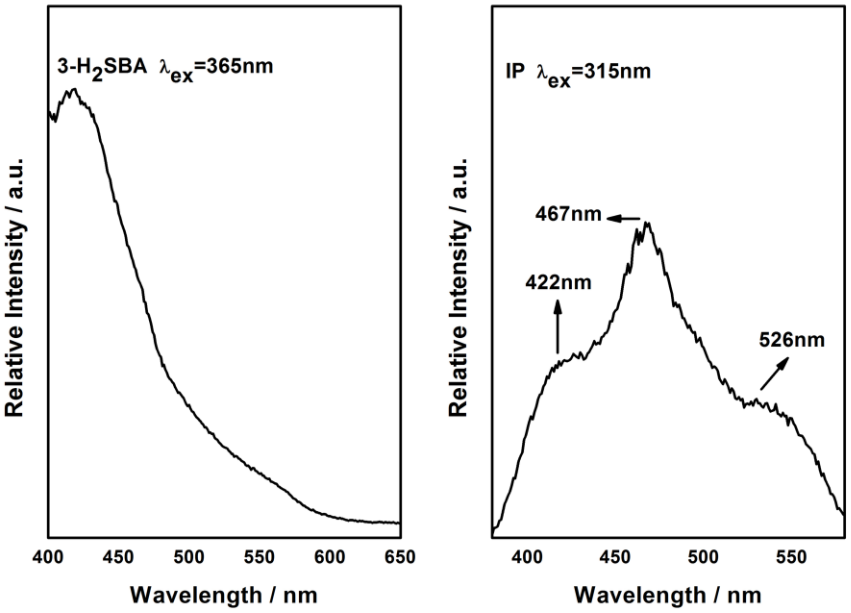


Figure S2. Emission spectra of 3-H_2SBA and IP.

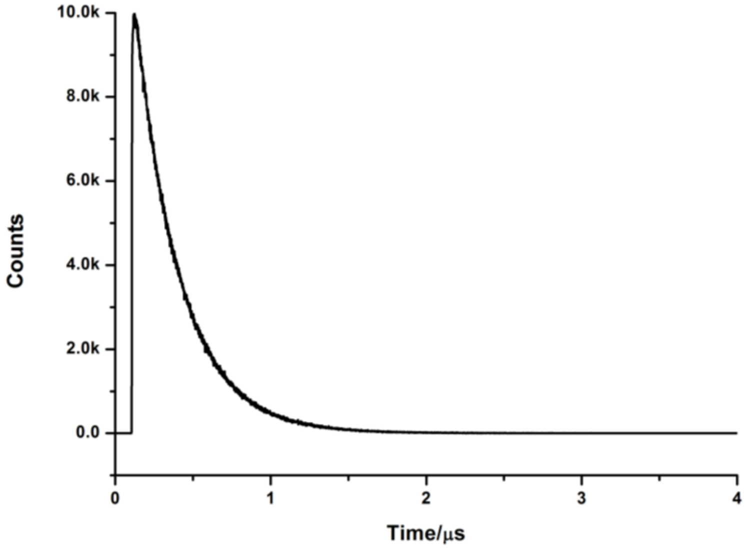


Figure S3. Decay profile of the complex **2**.

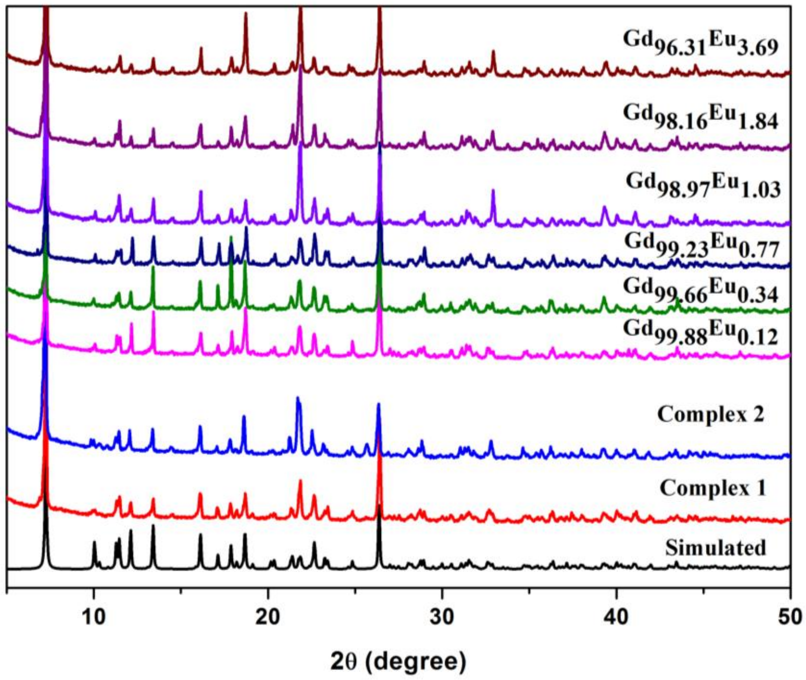
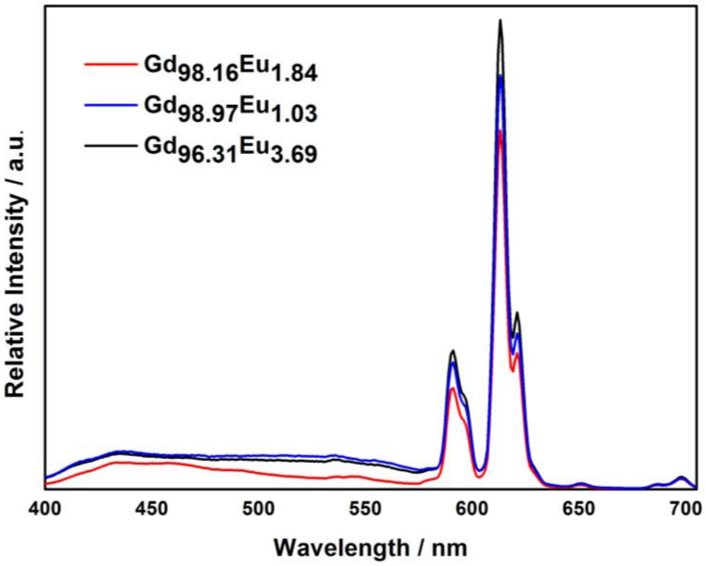
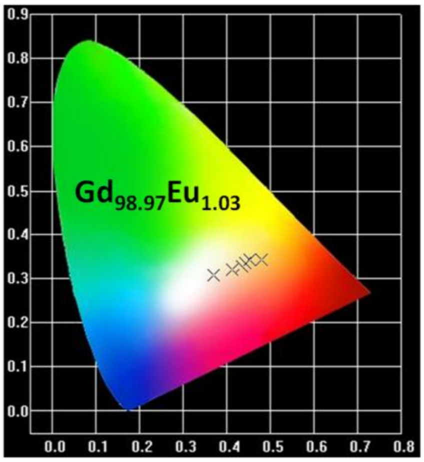


Figure S4. The PXRD patterns for complexes **1-2** and the doped complexes.



(a)



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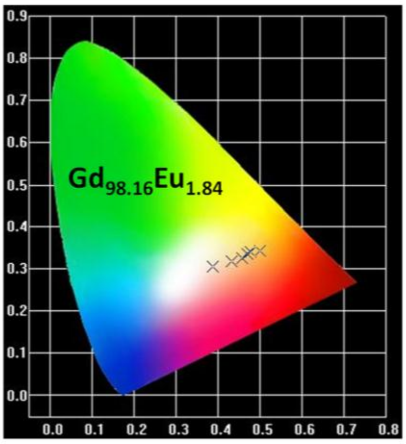
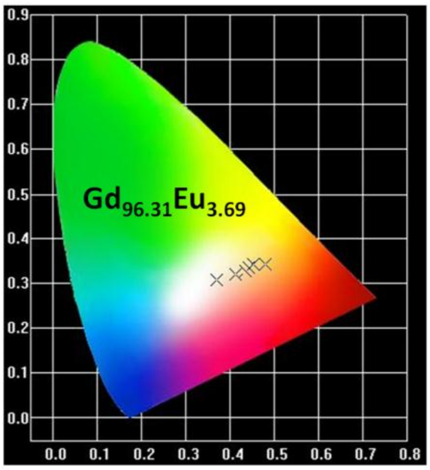


(c)



(d)

Figure S5. Emission spectra of the doped complexes excited at 380nm (a). The CIE chromaticity diagram of the doped complexes $Gd_{98.97}Eu_{1.03}$ (b), $Gd_{98.16}Eu_{1.84}$ (c) and $Gd_{96.31}Eu_{3.69}$ (d).

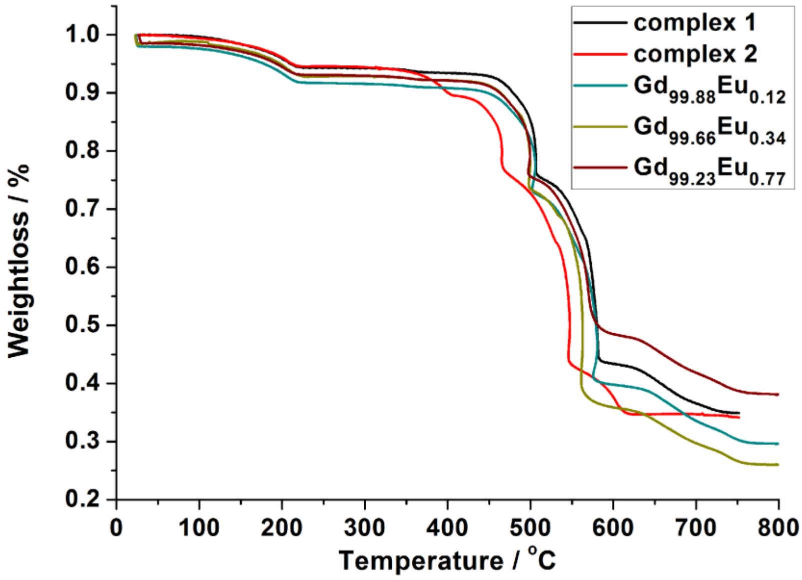


Figure S6. The TGA curves of the complexes **1**, **2** and doped complexes

Table S1. CIE chromaticity coordinates for the doped complexes excited at 320 to 395nm.

Excitation wavelength λ_{ex} / nm	CIE chromaticity coordinates (x, y) for the doped complexes		
	$Gd_{99.88}Eu_{0.12}$	$Gd_{99.66}Eu_{0.34}$	$Gd_{99.23}Eu_{0.77}$
320	(0.393, 0.363)	(0.398, 0.355)	(0.450, 0.360)
330	(0.374, 0.360)	(0.380, 0.352)	(0.430, 0.359)
340	(0.364, 0.360)	(0.372, 0.350)	(0.422, 0.359)
350	(0.359, 0.358)	(0.370, 0.347)	(0.423, 0.359)
360	(0.356, 0.353)	(0.367, 0.346)	(0.424, 0.358)
370	(0.348, 0.346)	(0.363, 0.345)	(0.416, 0.355)
375	(0.342, 0.341)	(0.361, 0.343)	(0.409, 0.352)
380	**(0.339, 0.339) A**	(0.359, 0.340)	(0.405, 0.350)
385	**(0.333, 0.336) B**	(0.353, 0.336)	(0.395, 0.346)
386	**(0.330, 0.335) C**	(0.350, 0.333)	(0.391, 0.344)
387	**(0.327, 0.333) D**	(0.345, 0.331)	(0.386, 0.342)
388	**(0.323, 0.330) E**	**(0.341, 0.328) F**	(0.380, 0.340)
389	(0.318, 0.328)	**(0.335, 0.325) G**	(0.374, 0.337)
390	(0.312, 0.324)	**(0.329, 0.322) H**	(0.366, 0.334)
391	(0.306, 0.321)	(0.321, 0.318)	(0.358, 0.331)
392	(0.299, 0.316)	(0.315, 0.316)	(0.349, 0.328)
393	(0.293, 0.312)	(0.308, 0.311)	**(0.341, 0.325) I**
394	(0.286, 0.308)	(0.300, 0.307)	**(0.332, 0.321) J**
395	(0.279, 0.303)	(0.293, 0.303)	(0.323, 0.318)

Table S2. The CIE chromaticity coordinates for the doped complexes excited at 320 to 395nm.

Excitation wavelength λ_{ex} / nm	CIE chromaticity coordinates (x, y) for the doped complexes		
	$Gd_{98.97}Eu_{1.03}$	**$Gd_{98.16}Eu_{1.84}$**	**$Gd_{96.31}Eu_{3.69}$**
320	(0.480, 0.343)	(0.500, 0.343)	(0.513, 0.315)
340	(0.452, 0.343)	(0.478, 0.339)	(0.486, 0.311)
360	(0.443, 0.335)	(0.469, 0.334)	(0.486, 0.309)
380	(0.434, 0.328)	(0.458, 0.325)	(0.472, 0.301)
390	(0.412, 0.321)	(0.432, 0.317)	(0.438, 0.290)
395	(0.369, 0.308)	(0.388, 0.304)	(0.385, 0.274)

Table S3. Crystal data and structure refinement for complexes **1-2**

Complex	**1**	**2**
Empirical formula	$C_{20}H_{17}N_4O_8SGd$	$C_{20}H_{17}N_4O_8SEu$
Formula weight	630.69	625.40
Crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å , °)		
a	9.6724(10)	9.6718(15)
b	10.0685(10)	10.0634(15)
c	12.6032(13)	12.5704(18)
α	76.167(2)	76.287(2)
β	79.590(2)	79.545(2)
γ	62.7200(10)	62.738(2)
Volume (Å^3)	1055.63(19)	1052.8(3)
Z	2	2
Calculated density / g· cm^{-3}	1.984	1.973
Absorption coefficient/ mm^{-1}	3.299	3.137
F(000)	618	616
Crystal size / mm^3	0.36×0.32×0.16	0.16×0.12×0.04
Θ range for data collection / (°)	2.38-27.69	2.31-25.25
Limiting indices	-11≦h≦11; -7≦k≦11; -10≦l≦14	-11≦h≦11; -12≦k≦8; -15≦l≦13
Reflections collected/unique	[R(int)= 0.0290] 5053 / 3627	[R(int)= 0.0313] 5389 / 3766
Data / restraints / parameters	5053 / 6 / 319	3766 / 6 / 323
Goodness-of-fit on F^2	1.027	1.047
Final R indices[I>2sigma(I)]	R1 = 0.0322 wR2 =0.0792	R1 = 0.0409 wR2 =0.0877
R indices(all data)	R1 = 0.0306 wR2 = 0.0781	R1 = 0.0476 wR2 = 0.0949

Largest difference peak and hole / e.Å^{-3}	2.142 and -1.611	0.821 and -1.021
CCDC	927215	927214

Table S4. Selected bond lengths [Å] and angles [°] for complexes **1-2**

		1	
Gd(1)-O(1)	2.422(3)	Gd(1)-O(2)	2.552(3)
Gd(1)-O(5B)	2.447(3)	Gd(1)-O(6)	2.444(3)
Gd(1)-O(7)	2.238(3)	Gd(1)-O(7A)	2.271(3)
Gd(1)-N(1)	2.583(3)	Gd(1)-N(4)	2.574(4)
O(7)-Gd(1)-O(7A)	69.72(11)	O(7)-Gd(1)-O(1)	93.67(12)
O(7A)-Gd(1)-O(1)	87.46(11)	O(7)-Gd(1)-O(6)	144.61(10)
O(7A)-Gd(1)-O(6)	145.50(10)	O(1)-Gd(1)-O(6)	92.01(13)
O(7)-Gd(1)-O(5B)	144.69(11)	O(7A)-Gd(1)-O(5B)	75.15(10)
O(1)-Gd(1)-O(5B)	81.23(12)	O(6)-Gd(1)-O(5B)	70.70(11)
O(7)-Gd(1)-O(2)	80.68(10)	O(7A)-Gd(1)-O(2)	128.35(11)
O(1)-Gd(1)-O(2)	52.50(10)	O(6)-Gd(1)-O(2)	74.34(12)
O(5B)-Gd(1)-O(2)	120.44(10)	O(7)-Gd(1)-N(4)	98.04(11)
O(7A)-Gd(1)-N(4)	81.19(11)	O(1)-Gd(1)-N(4)	159.70(12)
O(6)-Gd(1)-N(4)	88.00(12)	O(5B)-Gd(1)-N(4)	79.63(11)
O(2)-Gd(1)-N(4)	145.96(10)	O(7)-Gd(1)-N(1)	80.54(10)
O(7A)-Gd(1)-N(1)	129.58(10)	O(1)-Gd(1)-N(1)	135.41(11)
O(6)-Gd(1)-N(1)	71.12(11)	O(5B)-Gd(1)-N(1)	126.76(11)
O(2)-Gd (1)-N(1)	83.03(10)	N(4)-Gd(1)-N(1)	63.37(11)
		2	
Eu(1)-O(1)	2.436(5)	Eu(1)-O(2)	2.558(4)
Eu(1)-O(4B)	2.460(5)	Eu(1)-O(6)	2.448(4)
Eu(1)-O(7)	2.238(4)	Eu(1)-O(7A)	2.271(4)
Eu(1)-N(1)	2.582(5)	Eu(1)-N(4)	2.589(5)
O(7)-Eu(1)-O(7A)	69.5(2)	O(7)- Eu(1)-O(1)	93.51(17)
O(7A)- Eu(1)-O(1)	87.71(16)	O(7)- Eu(1)-O(6)	144.19(16)
O(7A)- Eu(1)-O(6)	146.24(16)	O(1)- Eu(1)-O(6)	91.43(17)
O(7)- Eu(1)-O(4B)	144.36(16)	O(7A)-Eu(1)-O(4B)	75.05(15)
O(1)- Eu(1)-O(4B)	81.75(16)	O(6)- Eu(1)-O(4B)	71.44(15)
O(7)- Eu(1)-O(2)	80.81(15)	O(7A)- Eu(1)-O(2)	128.14(15)
O(1)- Eu(1)-O(2)	51.94(15)	O(6)- Eu(1)-O(2)	74.57(16)
O(4B)- Eu(1)-O(2)	120.61(15)	O(7)- Eu(1)-N(4)	97.87(16)
O(7A)- Eu(1)-N(4)	81.30(16)	O(1)- Eu(1)-N(4)	160.26(16)
O(6)- Eu(1)-N(4)	88.74(17)	O(4B)- Eu(1)-N(4)	79.60(16)
O(2)- Eu(1)-N(4)	146.00(16)	O(7)- Eu(1)-N(1)	80.97(16)
O(7A)- Eu(1)-N(1)	129.31(16)	O(1)- Eu(1)-N(1)	135.60(16)
O(6)- Eu(1)-N(1)	70.96(16)	O(4B)- Eu(1)-N(1)	126.22(16)

O(2)- Eu(1)-N(1)	83.79(15)	N(4)- Eu(1)-N(1)	62.62(17)

Symmetry transformations used to generate equivalent atoms: For **1**, A: -x+1, -y+1, -z+2; B: -x+2, -y, -z+2. For **2**, A: -x, -y+1, -z+1; B: -x+1, -y, -z+1.

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References:

1. T. Smith; J. Guild, *Trans Opt*. *Soc*. 1931, ***33***, 73.

2. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Refinement, University of Göttingen (1997).

3. G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution, University of Göttingen (1997).