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Influence of the anion ratio in the composition of mixed benzoate/pentafluorobenzoate complexes of europium on the structure and photoluminescent properties

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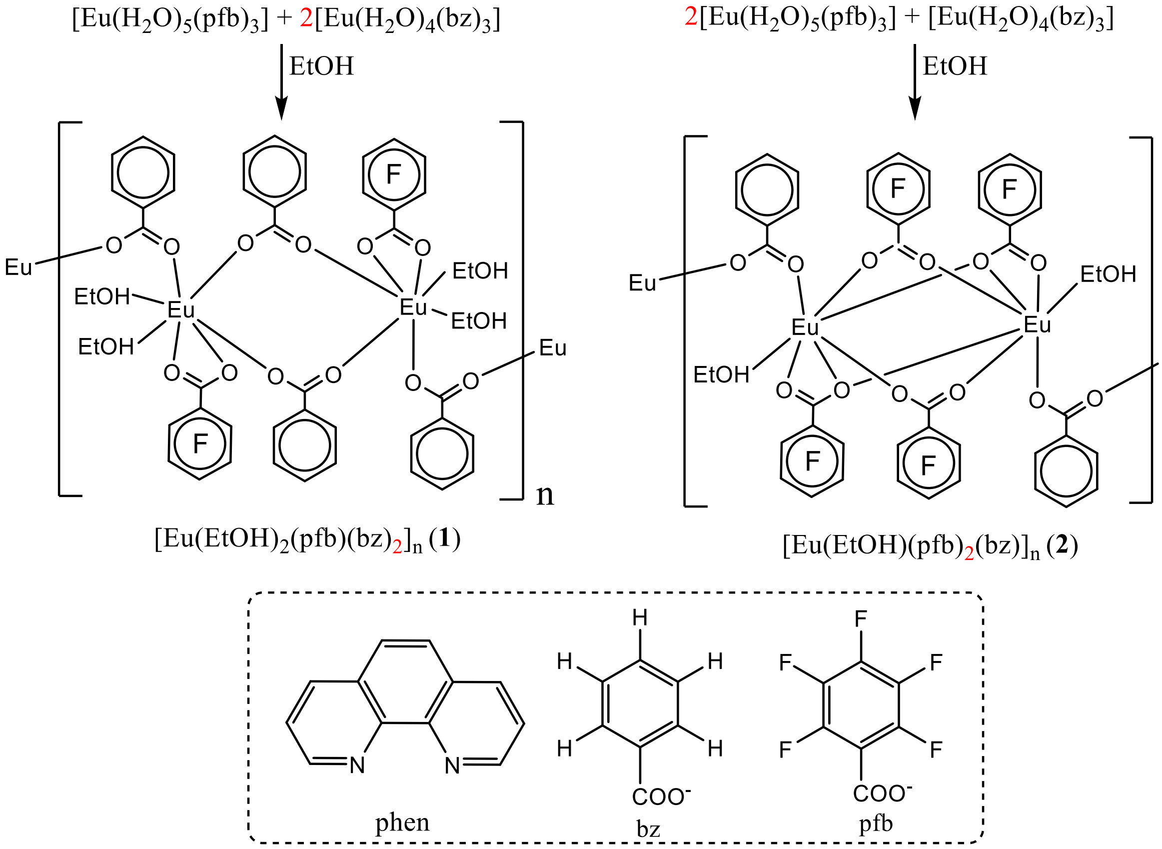
Contents

I. Synthetic data



Scheme S1. Synthesis of complexes **1** and **2**.

Synthesis of all obtained compounds was carried out in air using EtOH (96%). $[Eu(H_2O)_5(pfb)_3]$ and $[Eu(H_2O)_4(bz)_3]$ were synthesized using a known procedure[S1,S2].

Infrared spectra of the complexes were recorded in the frequency range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum 65 Fourier transform infrared spectrometer equipped with Quest ATR Accessory (Specac). Elemental CHNS analysis of the synthesized compounds was carried out on a EuroEA 3000 CHNS analyzer (EuroVector, S.p.A.).

The powder diffraction patterns were obtained using the Bruker D8 Advance diffractometer with a LynxEye detector in Bragg-Brentano geometry. The sample was finely dispersed on a silicon holder with a zero background, $\lambda(CuK\alpha) = 1.54060$ Å. The acquired data were refined using the Topas 4 software[S3].

Photoluminescence excitation, emission spectra, and luminescence decays were recorded at room temperature with a Horiba-Jobin-Yvon Fluorolog-QM spectrofluorimeter equipped with a 75 W ArcTune xenon lamp and a Hamamatsu R-FL-QM-R13456 photomultiplier sensitive in the 200-980 nm emission range. The luminescence quantum yield (Φ) values were measured by absolute method, employing the same setup equipped with a G8 Spectralon®- covered sphere (GMP SA, Switzerland) and Hamamatsu R13456 photomultiplier. A diffusing screen was mounted inside the sphere to avoid direct irradiation of the detector. The measurements were carried out at ambient temperature. The samples in quartz cells were placed near the center of the sphere. A NIST-traceable 45 W quartz tungsten-halogen bulb emission standard (Oriel) was employed to measure the instrument response function. All quantum yield (QY) measurements were repeated at least three times to achieve an experimental error below 15%.

Synthesis of $[Eu(EtOH)_2(pfb)(bz)_2]_n$ (1)

Europium(III) benzoate tetrahydrate (0.08 g, 0.136 mmol) was dissolved in 30 mL of ethanol under heating at 75°C with continuous stirring. Once the benzoate salt was completely dissolved, europium(III) pentafluorobenzoate pentahydrate (0.059 g, 0.067 mmol) was added to the solution. After the pentafluorobenzoate salt had also dissolved, the colorless solution was allowed to cool to room temperature (~25°C) and was then filtered into a tube-shaped Schlenk flask (100 mL). The volume of the filtered solution was reduced to 15 mL using vacuum evaporation. The flask was sealed and left undisturbed at room temperature (~25°C) to allow crystallization. Colorless needle-like crystals of compound **1**, suitable for X-ray diffraction analysis, formed after 3 weeks. The yield of compound **1** was 0.061 g (43.5%) based on $Eu(pfb)_3·5H_2O$.

Found, %: C 43.2; H 3.0.

For $EuC_{25}H_{22}F_5O_8$

Calculated, %: C 43.1; H 3.2.

IR-spectrum (ATR; ν, cm^{-1}): 3303 w, 2977 w, 1650 w, 1590 m, 1524 s, 1405 s, 1306 m, 1176 w, 1103 m, 1077 w, 1044 m, 994 m, 933 w, 877 w, 834 w, 768 m, 713 s, 670 m, 548 m, 509 m, 460 m, 416 s.

Synthesis of $[Eu(EtOH)(pfb)_2(bz)]_n$ (2)

Compound **2** was obtained by a procedure similar to that used in the synthesis of complex **1**. Europium(III) pentafluorobenzoate pentahydrate (0.100 g, 0.116 mmol) was dissolved in 15 mL of ethanol (EtOH) under heating at 75°C with continuous stirring. Once the salt was completely dissolved, additional ethanol was added to reach a total volume of 30 mL. Europium(III) benzoate tetrahydrate (0.035 g, 0.058 mmol) was then added to the solution. After complete dissolution, the colorless solution was allowed to cool to room temperature (~25°C) and was then filtered into a tube-shaped Schlenk flask (100 mL). The volume of the filtered solution was reduced to 10 mL using vacuum evaporation. The flask was sealed and left undisturbed at room temperature (~25°C) to allow crystallization. Colorless crystals of compound **2**, suitable for X-ray diffraction analysis, formed after 3 weeks. The yield of compound **2** was 0.05 g (57.8%) based on $Eu(pfb)_3·5H_2O$.

Found, %: C 37.1; H 1.2.

For $EuC_{23}H_{11}F_{10}O_7$

Calculated, %: C 37.3; H 1.5.

IR-spectrum (ATR; ν, cm^{-1}): 3617 w, 3069 w, 1650 m, 1590 m, 1548 s, 1527 m, 1493 s, 1391 s, 1298 m, 1259 w, 1181 w, 1109 m, 1035 m, 991 s, 934 m, 874 w, 826 w, 772 m, 740 m, 717 s, 668 m, 634 w, 559 m, 506 m, 434 w.

II. Supplementary PXRD data

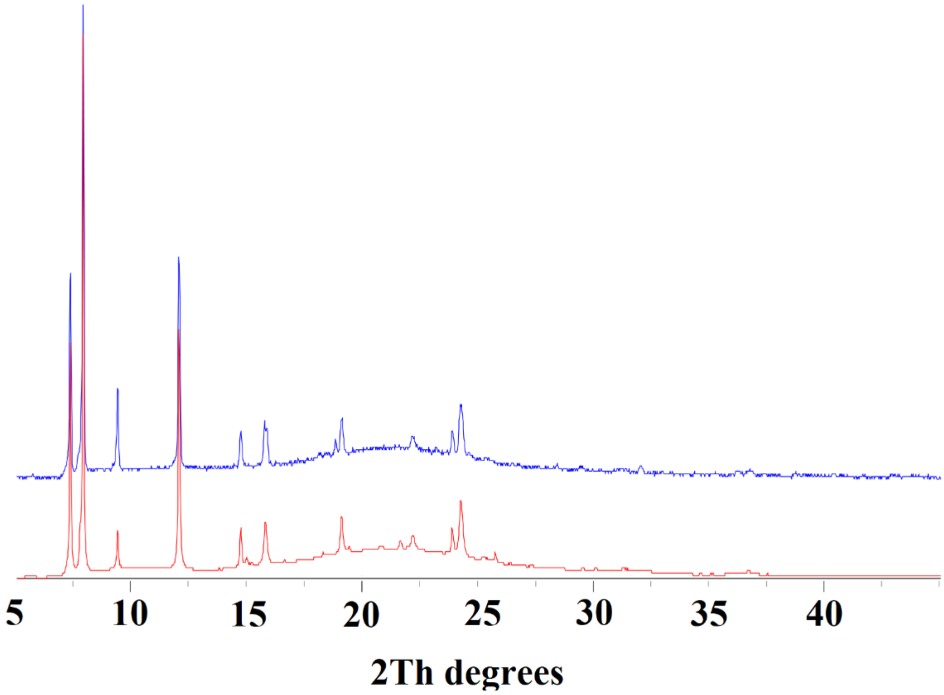


Figure S1. Theoretical (red line) and experimental (blue line) powder patterns of the compound **1** and their difference (grey line).

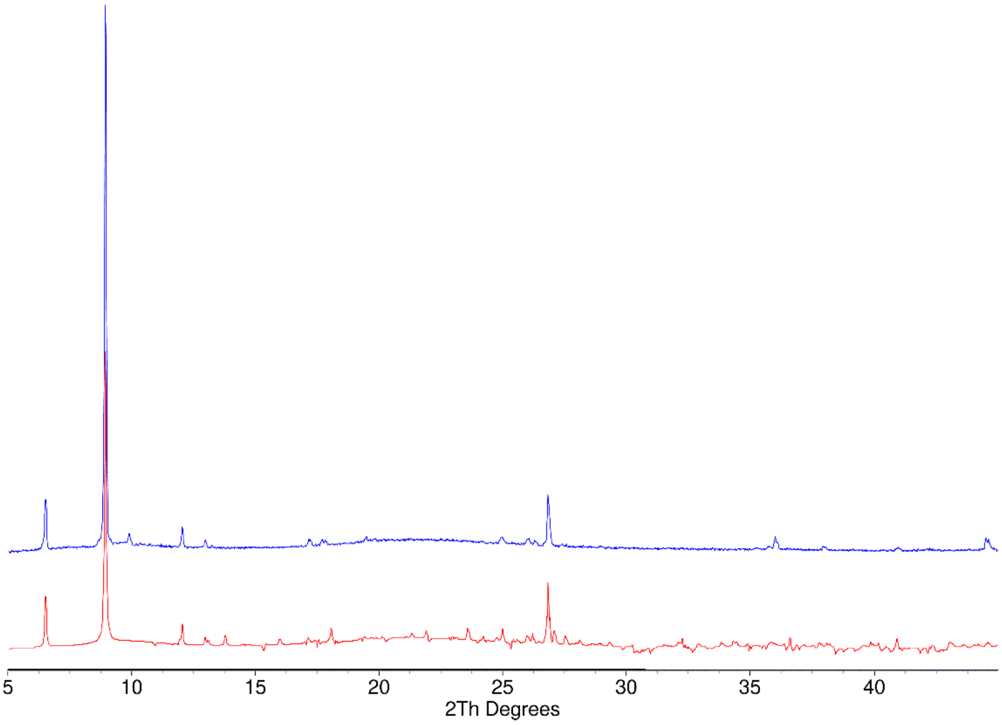


Figure S2. Theoretical (red line) and experimental (blue line) powder patterns of the compound 2 and their difference (grey line).

III. Supplementary structural data

Table S1 Basic geometric parameters of the complexes **1** and **2**.

Bond	Distance, Å	
	1	**2**
Eu-O (pfb)	2.542 (7), 2.570 (7)	2.372 (4)-2.579 (4)
Eu-O (bz)	2.311 (7), 2.353 (7)	2.278 (4), 2.306 (5)
Eu-O (EtOH)	2.460(7), 2.520(7)	2.419(5)
Eu···Eu	4.893(6), 4.980(7)	3.994(1), 5.374(2)
Angle, °		
Eu-Eu-Eu	153.85(4)	134.83(2)

Table S2. C-F···π interactions in the crystal packing of complexes **1** and **2**.

Interaction	F···Cg, Å	Symmetry code	F···Perp, Å	C-F···Cg,°
Complex **1**				
C(14)–F(14)···bz	3.703(10)		3.217	146.1(6)
C(12)–F(12)···pfb	3.508(10)	1-x,-y,-z	3.302	101.4(6)
Complex **2**				
C(4)–F(4)···bz	3.844(6)	1-x,1-y,1-z	3.817	74.8(3)
C(5)–F(5)···pfb	3.105(5)	2-x,-y,1-z	3.092	115.6(4)

Note. Cg is the centroid of aromatic rings, Perp is perpendicular to the plane of the ring, α is the angle between the planes of aromatic fragments.

Table S3. Hydrogen bonds in the crystal packing of complexes **1** and **2**.

Interaction	Distance, Å				D – H···A, º
	D–H	Symmetry code	H···A	D···A	
Complex **1**					
O(7)–H(7)···O(3)	0.86	2-x,1-y,1-z	1.95(4)	2.780(11)	162(6)
O(8)–H(8)···O(4)	0.85	1-x,1-y,1-z	2.24(9)	2.814(11)	125(6)
Complex **2**					
O(7)–H(7)···F(10)	0.84	-1+x,y,z	2.48	3.131(7)	135
C(17)–H(17)···F(14)	0.95		2.42	3.275(9)	149
C(22)–H(22A)···F(6)	0.99	2-x,-y,1-z	2.45	3.312(9)	145
C(22)–H(22B)···O(1)	0.99	1-x,-y,1-z	2.56	3.339(8)	136

Table S4. Continuous Shape Measures (CShM) values for the potential coordination polyhedron of Eu atoms in **1** and **2**.

	Eu
1	Triangular dodecahedron, D2d (2.077) Square antiprism, D4d (2.196) Biaugmented trigonal prism, C2v (2.302)
2	Triangular dodecahedron, D2d (1.215) Biaugmented trigonal prism, C2v (2.125) Square antiprism, D4d (2.705)

IV. Supplementary photoluminescent data

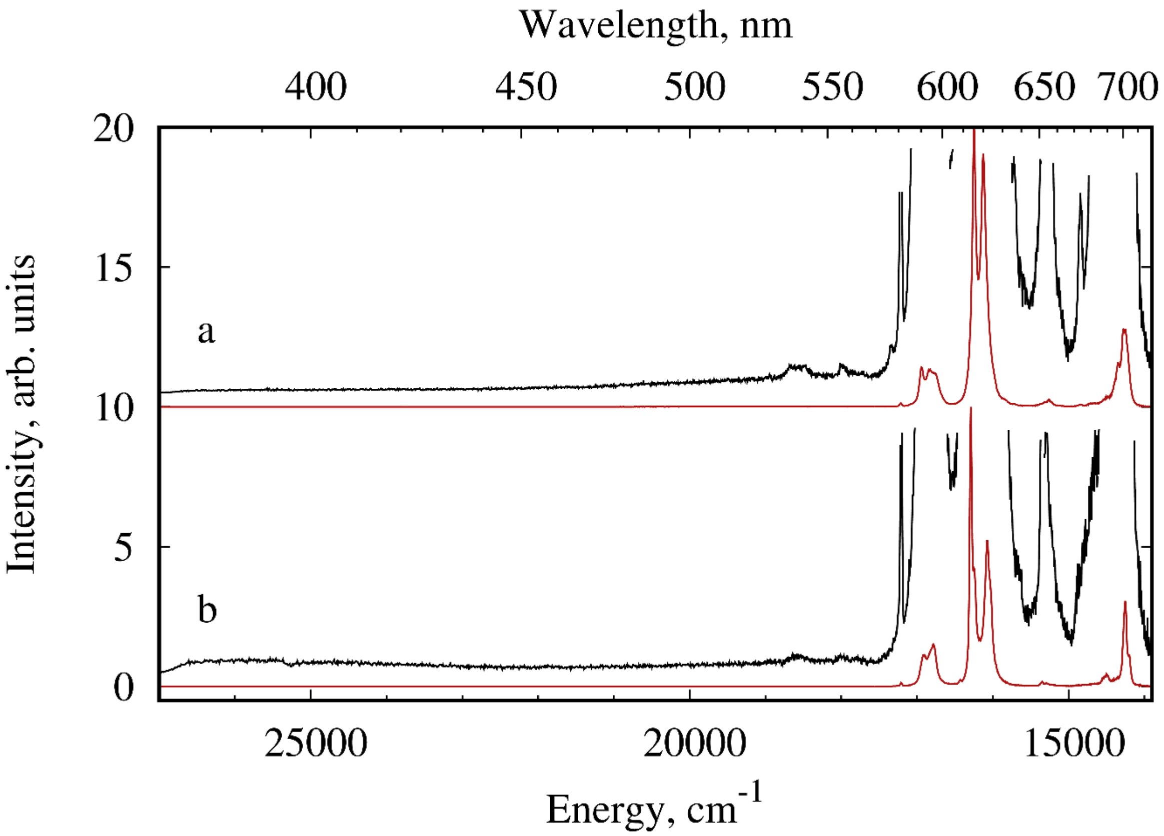


Figure S3. The emission spectra of complexes **1** (*a*) and **2** (*b*) obtained at *T* = 300 K under excitation at λ_{ex} = 280 nm. The black line shows the spectra on an enlarged scale.

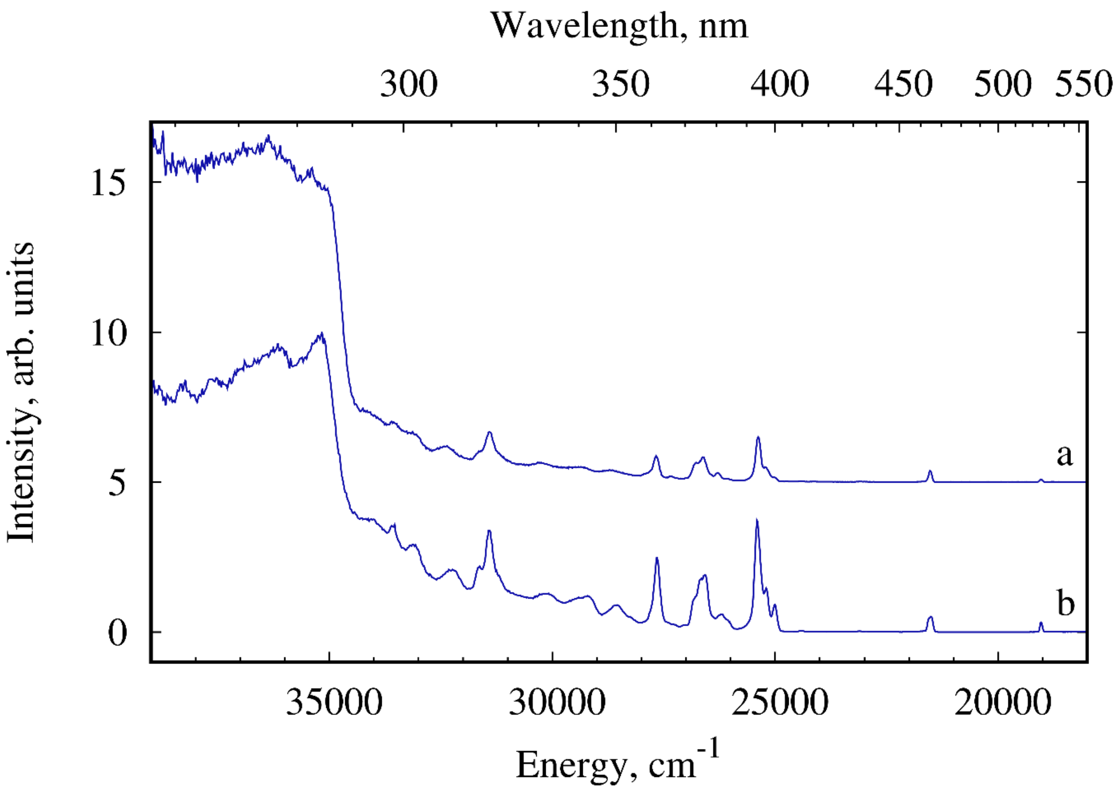


Figure S4. The excitation spectra of the **1** (*a*) and **2** (*b*) at λ_{em} = 615 nm and *T* = 77 K.

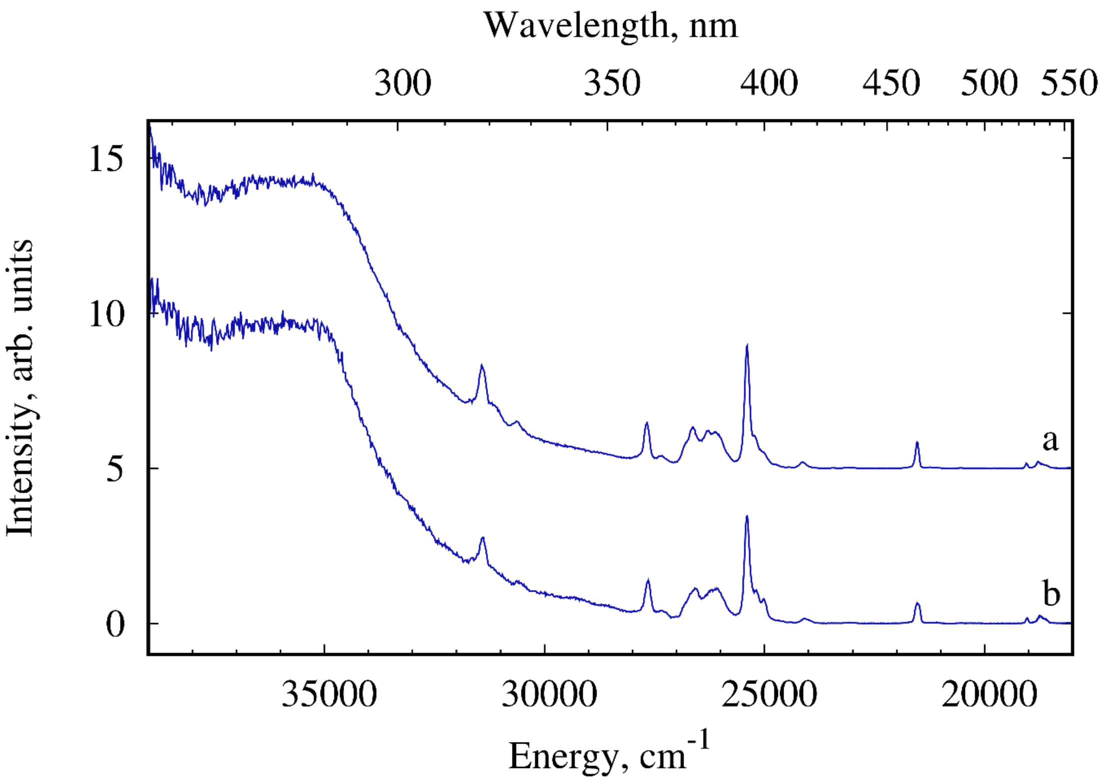


Figure S5. The excitation spectra of the complexes **1** (a) and **2** (b) at λ_{em} = 615 nm and *T* = 300 K.

V. References

S1. S. V. Larionov, L. A. Glinskaya, T. G. Leonova, R. F. Klevtsova, E. M. Uskov, V. E. Platonov, V. M. Karpov and V. P. Fadeeva, *Russ. J. Coord. Chem.*, 2009, **35**, 798; https://doi.org/10.1134/S1070328409110025.

S2. M. S. Khiyalov, I. R. Amiraslanov, F. N. Musaev and Kh. S. Mamedov, *Koordinatsionnaya Khimiya*, 1982, **8**, 548 (in Russian).

S3. N. V. Y. Scarlett and I. C. Madsen, *Powder Diffr.*, 2006, **21**, 278; https://doi.org/10.1154/1.2362855.