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Synthesis and structural characterization of the first europium(III) pyridylphosphine complex, [Eu(*N*,*N*′,*N*″-2-Py_3P)$(NO_3)_3$]

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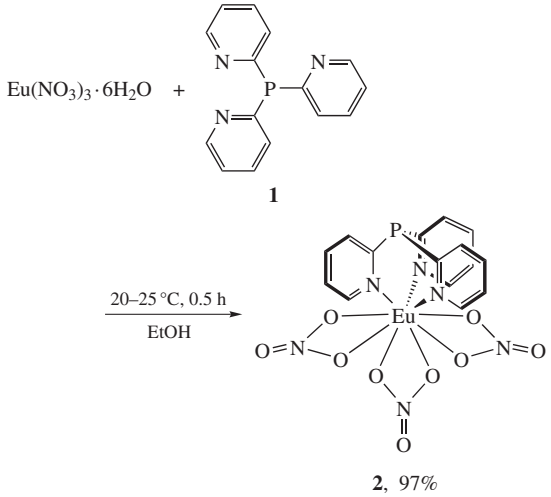
The first europium(III) pyridylphosphine complex, [Eu(*N*,*N*′,*N*″-2-Py_3P)$(NO_3)_3$] was prepared by the reaction between Eu$(NO_3)_3\cdot6H_2O$ and tris(2-pyridyl)phosphine; its structure was characterized by single-crystal X-ray diffraction.

Currently, pyridylphosphine ligands attract growing attention due to the simultaneous presence of the hard (pyridine nitrogen atom) and soft (phosphorus atom) centres, which make them desired in catalysis and materials chemistry.[1] Moreover, pyridylphosphines are reported as versatile intermediates in organic synthesis[2] and precursors for pharmaceuticals.[3] Among pyridylphosphines, tris(2-pyridyl)phosphine has got an increasing usage primarily owing to widespread flexibility in its coordination behaviour.[4] For instance, the *N*,*N*′,*N*″-coordination mode of tris(2-pyridyl)-phosphine, where the ligand binds to the metal *via* the three pyridyl nitrogen atoms,[5] has been observed in cases of Cr,[6] Mn,[7] Co,[8] Ni,[9] Cu,[10] Zn,[9(a),10(a),11] Mo,[12] Ru[13] and W.[14] Also, tris(2-pyridyl)phosphine can act as P,N-chelate or P,N-bridge ligand, what is specific for softer metals, such as Cu,[15] Mo,[16] Ru,[17] Rh,[17(a),18] Os,[19] Ir[20] and Pt.[18,21] A less favourable P-monodentate mode has been reported for complexes of Fe,[22] Rh,[16(b),23] Pd,[24] Pt,[25] Au[12,26] and Hg.[27] At the moment, only W,[14(a)] Tc[28] and Re[28] complexes, where tris(2-pyridyl)phosphine behaves as a N,N′-chelate ligand, are known. Similarly, rarer are the complexes containing *P*,*N*,*N*′-Py_3P ligand, the only example being [$RuCl(PPh_3)_2(Py_3P)$]X (X = Cl or PF_6).[29] As more exotic, N-monodentate coordination mode of the pyridylphosphine for the Al complex has been reported.[30]

Surprisingly, data on the pyridylphosphine complexes incorporating lanthanide ions are lacking in literature. Meanwhile, numerous lanthanide complexes are known to be remarkable luminescent and magnetic materials.[31] Special attention has been devoted to the Eu^{III} compounds, since their complexes generally exhibit unique photoluminescence properties.[32]

It might be expected that the merging of europium(III) ion with pharmacophore pyridylphosphine moieties in a one molecule may lead to the compounds exhibiting the beneficial properties of both these structural units. The goal of this work was to develop a synthesis of the first europium(III) pyridylphosphine complex using available[24(b),33] tris(2-pyridyl)phosphine ligand **1** and thoroughly characterize it by single-crystal X-ray diffraction, IR and NMR spectroscopy.

The complex [Eu(*N*,*N*′,*N*″-2-Py_3P)$(NO_3)_3$] **2** has been synthesized in quantitative yield by the reaction of Eu$(NO_3)_3\cdot6H_2O$ with tris(2-pyridyl)phosphine **1** in equimolar ratio (room temperature, 0.5 h, ethanol, Scheme 1).[†] The air- and moisture-stable complex **2** is well soluble in polar organic solvents and water. Single



Scheme 1

crystals of composition [Eu(*N*,*N*′,*N*″-2-Py_3P)$(NO_3)_3]\cdot CH_2Cl_2$, suitable for X-ray diffraction examination have been prepared by crystallization of complex **2** from an ethanol/dichloromethane solution.

Noteworthy, the reaction of Eu$(NO_3)_3\cdot6H_2O$ with two or three equivalents of pyridylphosphine **1** does not lead to formation of possible di-, [Eu$(NO_3)_3\cdot2Py_3P$], or tripyridylphosphine, [Eu$(NO_3)_3\cdot3Py_3P$], complexes. These results suggest that the

† *Synthesis of complex [Eu*(N,N′,N″-*2-Py$_3$P)(NO$_3$)$_3$]* **2**. To a solution of Eu$(NO_3)_3\cdot6H_2O$ (446 mg, 1.0 mmol) in ethanol (10 ml), tris(2-pyridyl)-phosphine (265 mg, 1.0 mmol) was added. The mixture was stirred for 30 min at room temperature until dissolution of tris(2-pyridyl)phosphine powder. The solvent was removed under reduced pressure, the residue was washed with diethyl ether (2×10 ml) and dried *in vacuo* (1 Torr, 45–50 °C) to afford complex **2** in 97% yield (585 mg), colourless crystals, mp > 240 °C (decomp.). ^{1}H NMR (400.13 MHz, D_2O) δ: 7.24–7.26 (m, 3H, H-5), 7.38–7.41 (m, 3H, H-3), 7.73–7.76 (m, 3H, H-4), 8.55–8.56 (m, H-6). ^{31}P NMR (161.98 MHz, D_2O) δ: –1.17. IR (KBr, ν/cm^{-1}): 3164, 3093, 3009, 2975, 2869, 1583, 1517, 1424, 1268, 1164, 1089, 1058, 1022, 1009, 812, 778, 740, 711, 637, 510, 493, 423. UV-VIS [EtOH, λ_{max}(log ε)]: 202 (4.42), 270 (4.04). Found (%): C, 29.77; H, 2.14; N, 13.79. Calc. for $C_{15}H_{12}EuN_6O_9P$ (%): C, 29.87; H, 2.01; N, 13.93. For more details, see Online Supplementary Materials.

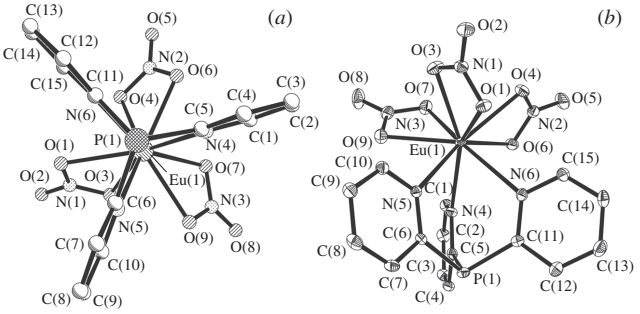


Figure 1 ORTEP diagrams of (*a*) molecular structure of **2**·CH_2Cl_2 and (*b*) molecular structure of this complex projected from the phosphorus atom to Eu^{III} ion. The solvent molecules and hydrogen atoms are omitted for clarity.

N,N′,N″-coordination mode of tris(2-pyridyl)phosphine, observed in monopyridylphosphine complex **2**, appears to be energetically more favourable than other possible coordination modes.

According to X-ray analysis, complex **2** crystallizes with one CH_2Cl_2 molecule in the monoclinic space group *Cc*.‡ Perspective views of the molecular structure of complex **2**·CH_2Cl_2 with the atom numbering schemes are shown in Figure 1.

The Eu^{III} ion is coordinated by three nitrogen atoms of the tris(2-pyridyl)phosphine ligand and six oxygen atoms of the three nitrate ligands to afford almost C_3 symmetrical half-sandwich structure. A pseudo-3-fold axis passes through the Eu and P atoms (see Figure 1). The coordination polyhedron of the nine-coordinate Eu^{III} ion can best be described as slightly distorted tricapped trigonal prism.

The pyridylphosphine **1** coordinated to the Eu^{III} ion acts as N,N′,N″-tripodal ligand. However, its geometry is distorted from ideal C_3 symmetry. Indeed, dihedral angles between the pyridine cycle planes of N(4)C(1)C(2)…C(5)/N(5)C(6)C(7)…C(10) = = 127.7°, N(4)C(1)C(2)…C(5)/N(6)C(11)C(12)…C(15) = 117.6° and N(5)C(6)C(7)…C(10)/N(6)C(11)C(12)…C(15) = 114.6°. As observed for the free tris(2-pyridyl)phosphine,[34] the P(1) atom in complex **2** adopts a slightly distorted pyramidal geometry and out of the C(5)C(6)C(11) plane by 0.82 Å. Similarly, the C–P–C angles of C(6)–P(1)–C(11) = 99.4(2)°, C(6)–P(1)–C(5) = = 104.2(2)° and C(11)–P(1)–C(5) = 102.0(2)° are not equivalent. The C–P bond distances lie in the range 1.840–1.845 Å, comparable to 1.824–1.834 Å in free tris(2-pyridyl)phosphine ligand.[34] The three N(pyridine)–Eu–N(pyridine) angles at the Eu^{III} center of N(5)–Eu(1)–N(6) = 75.1(1)°, N(5)–Eu(1)–N(4) = = 78.0(1)° and N(4)–Eu(1)–N(6) = 76.3(1)° are unequal. The three Eu–N(pyridine) bonds are almost equal in lengths (2.514, 2.540 and 2.564 Å), which are comparable to those observed in the Eu^{III} complexes with other pyridine-based ligands.[35] As follows from the Eu(1)–P(1) distance [3.932(1) Å], there is no transannular interaction between phosphorus atom and Eu^{III} ion.

Each of the three nitrate ligands coordinated to Eu^{III} ion is essentially planar and acts as a bidentate chelating ligand. The dihedral angles between nitrate group planes are 93.5°, 90.3° and 85.1°. The average Eu–O distances (2.466 Å) are comparable with the corresponding values in the reported Eu^{III} nitrate complexes.[35(*b*),(*c*)] The average O–Eu–O nitrate bite angles (51.79°) fall close to the values found in the similar lanthanide(III) nitrate complexes.[35(*b*),(*c*)] Likewise, the nitrate bite distances in the range of 2.3509(5)–2.3600(9) Å are normal.[35(*b*),(*c*)]

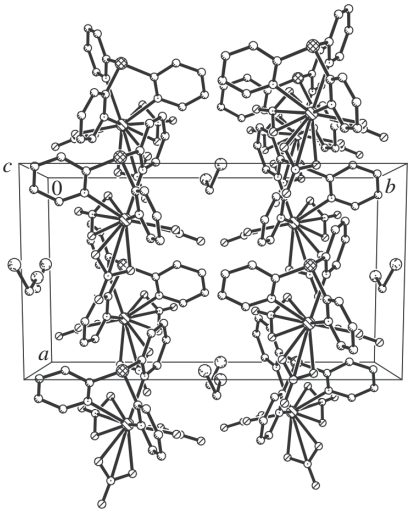


Figure 2 Partial packing diagram of the complex **2**·CH_2Cl_2 with solvent molecules. Hydrogen atoms are omitted for clarity.

The crystal packing diagram of [Eu(2-Py_3P)$(NO_3)_3$]·CH_2Cl_2 is shown in Figure 2.

The solid-state IR spectrum of complex **2** exhibits strong absorption bands in the range of 1600–900 cm^{-1}. Stretching vibration of the N–O bonds appearing as strong doublet (1506, 1491 cm^{-1}), strong triplet (1316, 1292, 1276 cm^{-1}) and moderate doublet (1044, 1026 cm^{-1}) corresponds to bidentate nature of the nitrate ligand. Three doublets at the same regions (1536, 1517, 1268, 1236, 1021, 1009 cm^{-1}) confirm the preserving the Eu$(NO_3)_3$ moieties. The higher frequency shifts of the planar deformation vibration bands of the pyridine ring and its out-of-plane deformation vibrations from 618 and 417 cm^{-1} in the spectrum of ligand up to 673 and 423 cm^{-1} in the spectrum of complex **2** are typical of pyridine complexes.[36] In addition, the participation of pyridine nitrogen atoms in the coordination with Eu^{III} ion is accompanied by the higher frequency shift of the stretching doublet of the pyridine ligand from 1572 and 1559 cm^{-1} to 1583 cm^{-1} in complex **2**.

The solution state behaviour of complex **2** was studied using ^1H and ^{31}P NMR spectroscopy at room temperature. The ^1H NMR spectrum of the compound in D_2O shows the usual peaks of 2-pyridine moieties in their characteristic regions.† The ^{31}P NMR spectrum of complex **2** in D_2O exhibits a sharp peak at –1.17 ppm. Note that NMR spectra of complex **2** are almost identical to those of free tris(2-pyridyl)phosphine ligand **1**[33] testifying the great lability of the complex in solution at room temperature.

In summary, in the europium(III) pyridylphosphine complex, [Eu(*N*,*N*′,*N*″-2-Py_3P)$(NO_3)_3$], metal centre is coordinated to the three pyridine moieties of the ligand in a *N*,*N*′,*N*″-tripodal mode. The results contribute to the coordination chemistry of europium as well as to the chemistry of pyridine and phosphines. The investigation of luminescence of complex **2** is under way and the results will be published elsewhere.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.11.004.

‡ *Crystallographic data for* **2**. Crystals of **2**·CH_2Cl_2 ($C_{15}H_{12}EuN_6O_9P$·CH_2Cl_2, M = 688.16) are monoclinic, space group *Cc*, a = 10.2858(9), b = 17.856(2) and c = 12.829(1) Å, β = 101.214(1)°, V = 2311.3(3) $Å^3$, Z = 4, d_{calc} = 1.98 g cm^{-3}, μ(MoKα) = 3.075 mm^{-1}, T = 173 K, 8911 reflections measured, 4969 independent reflections (R_{int} = 0.0281), R_1 = = 0.0257 for 4694 reflections with $I > 2\sigma(I)$, wR_2 = 0.0567. For more details, see Online Supplementary Materials.

CCDC 869847 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

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