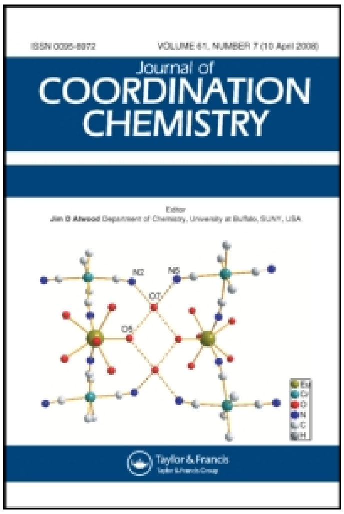

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EUROPIUM(III) PICRATE COMPLEXES WITH α-(DIETHOXYPHOSPHORYL)-PROPANONE AND DIETHYL-1-METHYLVINYLPHOSPHATE: SYNTHESES, SPECTROSCOPY AND STRUCTURES

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The Eu(III) picrate complexes with the isomers α-(diethoxyphosphoryl)propanone and diethyl-1-methylvinylphosphate were synthesized and characterized by elemental analyses, IR spectroscopy and emission spectroscopy. X-ray single crystal analyses show that in both complexes the picrate anions are bidentate, bonded through the phenolic and one *o*-nitrogroup oxygens. The neutral ligands are bonded only through their phosphoryl oxygens, resulting in tricapped trigonal prism coordination polyhedra with C_{3v} symmetry.

Keywords: Complexes; europium; picrate; α-(diethoxyphosphoryl)propanone; diethyl-1-methylvinylphosphate

INTRODUCTION

A series of lanthanide picrate complexes with organic sulfoxides,[1–7] phosphine oxide[8,9] N-oxides,[4,10–12] amides,[4,13–16] phosphoramides[17,18] and lactams[19,20] have been reported. In particular, complexes between europium(III) picrate and phosphoryl neutral ligands[9] have intense luminescence, thus being candidates to phosphors.

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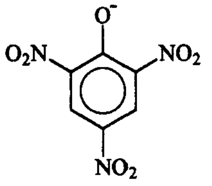
This work relates the syntheses, characterization and structures of europium(III) picrates (pic, **1**) with α-(diethoxyphosphoryl)propanone (DEPP, **2**) and diethyl-1-methylvinylphosphate (DMVP, **3**), which are keto-enol isomers. It is worth noting that DEPP could coordinate through either the phosphoryl and carbonyl oxygens, which was not the case, as will be seen below.



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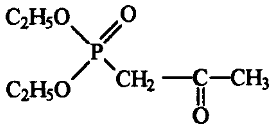

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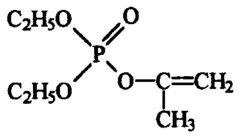

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EXPERIMENTAL

Instrumentation

Elemental analyses (CHN) were carried out on a Perkin-Elmer 240 elemental analyzer. IR spectra of the solid complexes were recorded on a Perkin-Elmer 1750 FTIR spectrometer, using KBr pellets. IR spectra of the ligands were obtained on a Nicolet Magna 550 FTIR spectrometer, using $10^{-2}\,\mathrm{mol\,L^{-1}}$ solutions in carbon tetrachloride and a 0.519 mm sodium chloride cell. Proton NMR spectra were recorded on a Bruker AC-200 spectrometer, using deuterochloroform as solvent and TMS as an internal standard. Emission spectra were recorded in a modified Hitachi MPF4 spectrofluorimeter.

Ligand Syntheses

The ligands were synthesized by an adaptation of the method described for obtaining S-ethyl-α-diethoxyphosphoryl-thioacetates,[21] reacting equimolar quantities of triethylphosphite with bromoacetone[22] in benzene at room temperature, followed by reflux for 7 h.

α-(Diethoxyphosphoryl)propanone and diethyl-1-methylvinylphosphate were obtained in 56 : 44 ratio. The isomers were separated in a silica gel chromatographic column, using hexane/acetone (75 : 25) as eluent.

Distillation of DEPP under reduced pressure (79°C at 8 Torr,[23] 126°C at 9 Torr) afforded purified DEPP in 39% yield. This product was characterized by IR absorption spectroscopy in CCl_4 ($\nu CO = 1719\,cm^{-1}$; $\nu PO = 1255\,cm^{-1}$) and proton NMR in $CDCl_3$ ($\delta = 1.35$ ppm, $OCH_2C\underline{H}_3$; 2.33, $COC\underline{H}_3$; 4.20, $OC\underline{H}_2CH_3$).

DMVP was distilled at 72°C (1.1 Torr)[23] with a 31% yield and characterized also by IR ($\nu C{=}C = 1661\,cm^{-1}$; $\nu PO = 1274\,cm^{-1}$) and proton NMR ($\delta = 1.36$ ppm, $OCH_2C\underline{H}_3$; 1.94, $COC\underline{H}_3$; 4.17, $OC\underline{H}_2CH_3$; 4.50, $C{=}C\underline{H}_2$; 4.76, $C{=}C\underline{H}_2$).

Complex Syntheses

Europium(III) picrate was obtained by reaction of picric acid with Eu(III) basic carbonate in water, using a small excess of the latter. This solution was filtered, partially evaporated and left to crystallize at room temperature for 24 h. The crystals were separated by filtration and allowed to dry in air at room temperature.

Europium(III) picrate was dissolved in ethanol (absolute) and the ligands added as liquids in a 3 : 1 molar ratio. The solutions were left to crystallize at room temperature. The solids were filtered, washed with a small volume of absolute ethanol and dried in air over filter paper. Observed yields were 85% and 78% for the DEPP and DMVP complexes, respectively.

X-ray Crystallography

Suitable crystals were mounted on glass fibre and aligned on an Enraf-Nonius CAD-4 Mach3 diffractometer for data collection. Cell parameters were determined on the basis of 25 reflections with $9.62 < \theta < 17.50°$ and $9.69 < \theta < 18.80°$ for DEPP and DMVP, respectively. Intensity data were obtained with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) and $\omega - 2\theta$ scan mode in the range $3.72 < \theta < 25.02°$ and $2.11 < \theta < 25.55°$ for DEPP and DMVP, respectively, at room temperature. During data collection, the intensity of three standard reflections monitored every 1800s of X-ray exposure showed no significant decay. Data were corrected for Lorentz and polarization effects; an empirical absorption correction based on a series of PSI scans was applied to the data. Relative transmission coefficients ranged from 0.5532 to 0.9984 and from 0.5589 to 0.9986, for DEPP and DVMP, respectively. Structures were solved by the standard heavy atom Patterson method (SHELX-86),[24] followed by normal difference Fourier techniques that yielded the positions of all remaining non-H atoms. H-atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom. Due to the rather poor diffraction quality of the crystals only the heavy atoms of the pic groups and the P–O moiety were refined anisotropically by full-matrix least-squares methods on F^2 (SHELXL93).[25] Molecular displays were performed by ZORTEP.[26]

RESULTS AND DISCUSSION

Elemental analyses for the DEPP complex, C 32.5% (33.0% theoretical); H 3.2% (3.6); N 8.7% (8.9). For the DMVP complex, C 32.6% (32.6); H 3.6% (3.7), N 8.9% (8.8). These results indicate compositions $Eu(pic)_3 \cdot 3(DEPP)$ and $Eu(pic)_3 \cdot 3(DMVP) \cdot H_2O$ for the complexes.

Infrared absorption spectra of the DEPP complex show the picrate ion characteristic frequencies: $\nu_s NO_2$ (1366 and 1329 cm^{-1}) and $\nu_{as} NO_2$ (1579 and 1542 cm^{-1}). These frequencies in the DMVP complex are: $\nu_s NO_2$ (1366 and 1329 cm^{-1}) and $\nu_{as} NO_2$ (1580 and 1541 cm^{-1}). These results suggest that the picrate anions are bidentate and bonded through the phenolic and one *o*-nitrogroup oxygens in both cases.[27] A characteristic water band at *ca.* 3500 cm^{-1} also appeared in the DMVP complex.

Table I shows some relevant IR absorption frequencies related to the neutral ligands. It can be observed that νCO (for DEPP) and νC=C (for DMVP) in the complexes, with relation to the free ligands, follow different trends. $\Delta\nu$ for νPO in both complexes is *ca.* -13 cm^{-1}, whereas νCO and νC=C increase by *ca.* 4 cm^{-1}. This negative shift of νPO indicates bonding through the phosphoryl oxygens.[9] On the other hand, taking into account this bonding, the polarization of the PO group is changed, increasing the positive formal charge at the phosphorus atom. This gives rise to an attractive inductive effect ($-$I), which in turn decreases the polarization of

TABLE I Relevant infrared absorption frequencies of the complexes and neutral free ligands (cm^{-1})

	Eu(pic)$_3$ · 3(DEPP)	*Free ligand*	$\Delta\nu$[a]
νPO	1241	1255	−14
νCO	1722	1719	+3
	Eu(pic)$_3$ · 3(DMVP)	*Free ligand*	$\Delta\nu$
νPO	1261	1274	−13
νC=C	1666	1661	+5

[a] $\Delta\nu$ refers to the difference: ν(complex) − ν(free ligand).

the carbonyl group (in the DEPP complex) and also increases the C=C double bond character (in the DMVP complex), due to the decreasing contribution of the [$-O^+{=}C-C^-$] resonance structure with relation to [$-O-C{=}C$], causing a slight increase in the frequencies of the C=O and C=C oscillators, in comparison with the free ligands.

The basicity of phenol associated with the phosphoryl group of diethylethylphosphonate (evaluated by $\Delta\nu OH = 398\,cm^{-1}$)[28] is almost twice that observed for phenol with aliphatic ketones ($\Delta\nu OH = 210\,cm^{-1}$).[29] Therefore, the higher basicity of the phosphoryl oxygen explains the exclusive coordination of DEPP through this group, as observed in the X-ray single-crystal analyses, discussed below.

It should be stressed that, as the basicity of the phosphoryl oxygen is considerably higher than that of the π-electron system of the vinyl group in DMVP, coordination exclusively through this oxygen is expected, as confirmed by the crystal structure.

Both complexes have intense luminescence, and may be interesting phosphors. The emission spectra are shown in Figure 1. Peaks were assigned as follows:[30] the DEPP complex at 77 K displays one $^5D_0 \rightarrow {}^7F_0$ peak (579 nm), three $^5D_0 \rightarrow {}^7F_1$ (589.7, 591.5 and 595 nm) and four peaks for the $^5D_0 \rightarrow {}^7F_2$ transition (614, 614.8, 615.7 and 617 nm). The DMVP complex at 77 K

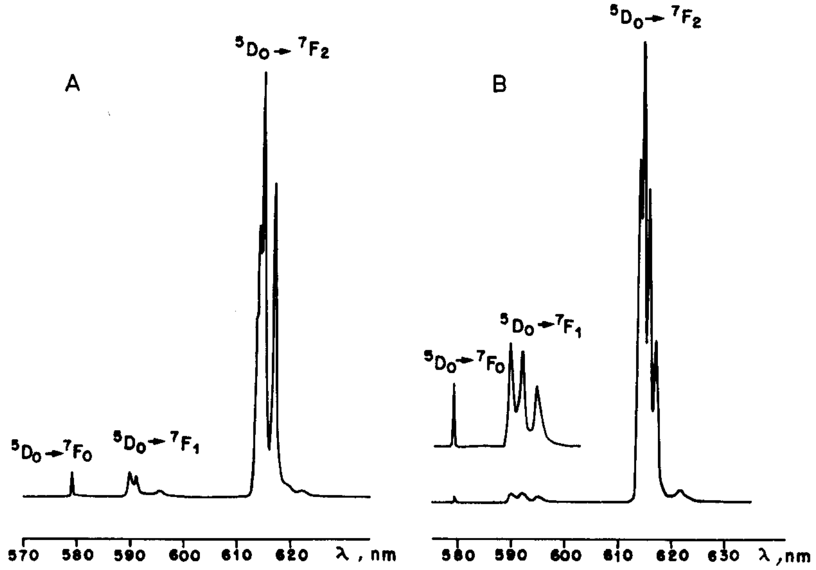

FIGURE 1 Emission spectra at 77 K. A: Eu(pic)$_3$ · 3DMVP; B: Eu(pic)$_3$ · 3DEPP.

presents one $^5D_0 \rightarrow {}^7F_0$ peak (579 nm), three $^5D_0 \rightarrow {}^7F_1$ (589.5, 591.5 and 596 nm) and four $^5D_0 \rightarrow {}^7F_2$ (614, 615, 617 and a shoulder at 613.5 nm).

From these results, it is evident that both emission spectra are very similar. Taking into account the stoichiometry and that the crystal field causes a Stark splitting of the $^7F_1$ level into three components (one A_2 and two E species) and the $^7F_2$ into four (one A_1 and two 2E, one of the latter split into two components), C_{3v} symmetry can be suggested for both coordination polyhedra.[31]

X-ray single-crystal analyses were performed for both complexes. Table II presents the crystallographic parameters and Table III selected bond distances and angles. Atomic position parameters and supplementary data have been deposited with the editor and are available from P.C.I.

From these data, it is apparent that both coordination polyhedra are similar and are tricapped trigonal prisms, in agreement with the luminescence data. One base of the prism contains the phenolic oxygens of the picrate anions; the *o*-nitrogroup oxygens are the caps and the phosphoryl

TABLE II Summary of data collection and crystal parameters

	DEPP	*DVMP*
Empirical formula	$C_{39}H_{51}EuN_9O_{33}P_3$	$C_{39}H_{53}EuN_9O_{34}P_3$
Formula weight	1418.76	1436.77
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Unit cell dimensions	$a = 12.718(1)$ Å	12.7339(9) Å
	$b = 13.485(1)$ Å	13.517(1) Å
	$c = 20.068(2)$ Å	20.118(2) Å
	$\alpha = 72.98(1)°$	72.81(1)°
	$\beta = 85.26(1)°$	85.216(8)°
	$\gamma = 64.83(1)°$	64.840(7)°
Volume	2975.0(6) Å^3	2990.7(4) Å^3
Z	2	2
Density (calculated)	1.584 mg/m^3	1.596 mg/m^3
Absorption coefficient	1.234 mm^{-1}	1.230 mm^{-1}
F(000)	1440	1460
Crystal size	0.35 × 0.20 × 0.20 mm	0.30 × 0.18 × 0.15 mm
θ range	3.72–25.02°	2.11–25.55°
Index ranges	$0 \leq h \leq 15, -14 \leq k \leq 16, -23 \leq l \leq 23$	$-15 \leq h \leq 13, -16 \leq k \leq 0, -24 \leq l \leq 23$
Reflections collected	11749	11638
Independent reflections	10404 [$R_{int} = 0.0774$]	11134 [$R_{int} = 0.0286$]
Refinement method	Full-matrix least-squares on F^2	
Data/parameters	10399/625	11132/634
Goodness-of-fit on F^2	1.023	1.054
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0949$, w$R2 = 0.2387$	$R1 = 0.0903$, w$R2 = 0.2344$

TABLE III Distances (Å) and angles (°) around the europium ions

	DEPP	*DMVP*
Eu O1	2.333(10)	2.351(7)
Eu O3	2.363(9)	2.369(8)
Eu O2	2.354(10)	2.353(7)
Eu O11	2.344(9)	2.354(6)
Eu O21	2.336(8)	2.332(5)
Eu O31	2.333(10)	2.345(7)
Eu O111	2.608(10)	2.597(6)
Eu O211	2.628(11)	2.621(7)
Eu O311	2.605(13)	2.616(8)
O3 Eu O21	135.9(4)	135.6(2)
O3 Eu O11	139.9(4)	139.4(2)
O21 Eu O11	77.7(3)	77.9(2)
O3 Eu O31	86.8(4)	86.7(3)
O21 Eu O31	77.9(3)	77.2(2)
O11 Eu O31	79.6(3)	79.3(2)
O3 Eu O2	79.8(4)	80.0(3)
O21 Eu O2	83.6(4)	83.2(2)
O31 Eu O2	136.5(4)	135.5(2)
O3 Eu O1	79.7(4)	79.5(3)
O21 Eu O1	138.5(4)	138.9(2)
O11 Eu O1	83.4(4)	84.0(3)
O31 Eu O1	134.4(4)	135.1(3)
O2 Eu O1	83.6(4)	83.9(3)
O3 Eu O211	70.7(4)	70.3(2)
O21 Eu O211	65.2(3)	65.4(2)
O11 Eu O211	134.6(3)	134.5(2)
O31 Eu O211	68.2(4)	67.4(2)
O2 Eu O211	68.3(4)	68.1(2)
O1 Eu O211	142.0(4)	141.5(3)
O3 Eu O311	71.4(4)	71.0(3)
O21 Eu O311	133.0(3)	133.2(2)
O11 Eu O311	68.6(3)	68.5(3)
O31 Eu O311	64.9(4)	65.6(3)
O2 Eu O311	143.3(4)	143.5(3)
O1 Eu O311	69.5(4)	69.6(3)
O211 Eu O311	120.0(4)	119.4(3)
O3 Eu O111	138.4(4)	138.8(2)
O21 Eu O111	68.6(3)	68.5(2)
O11 Eu O111	64.7(3)	65.2(2)
O31 Eu O111	134.8(3)	134.5(2)
O2 Eu O111	69.4(3)	69.6(2)
O1 Eu O111	69.9(4)	70.5(2)
O211 Eu O111	119.2(4)	119.4(2)
O311 Eu O111	120.1(4)	120.6(2)

oxygens of the neutral ligands (DEPP and DMVP) form the other base of the prism. In both cases the bases are parallel, to within experimental accuracy, the dihedral angle being 2(1)°. Figure 2 shows the ZORTEP view of the DMVP and Figure 3 the DEPP complex. Figures 4 and 5 show the coordination polyhedra of the DMVP and DEPP complexes, respectively.

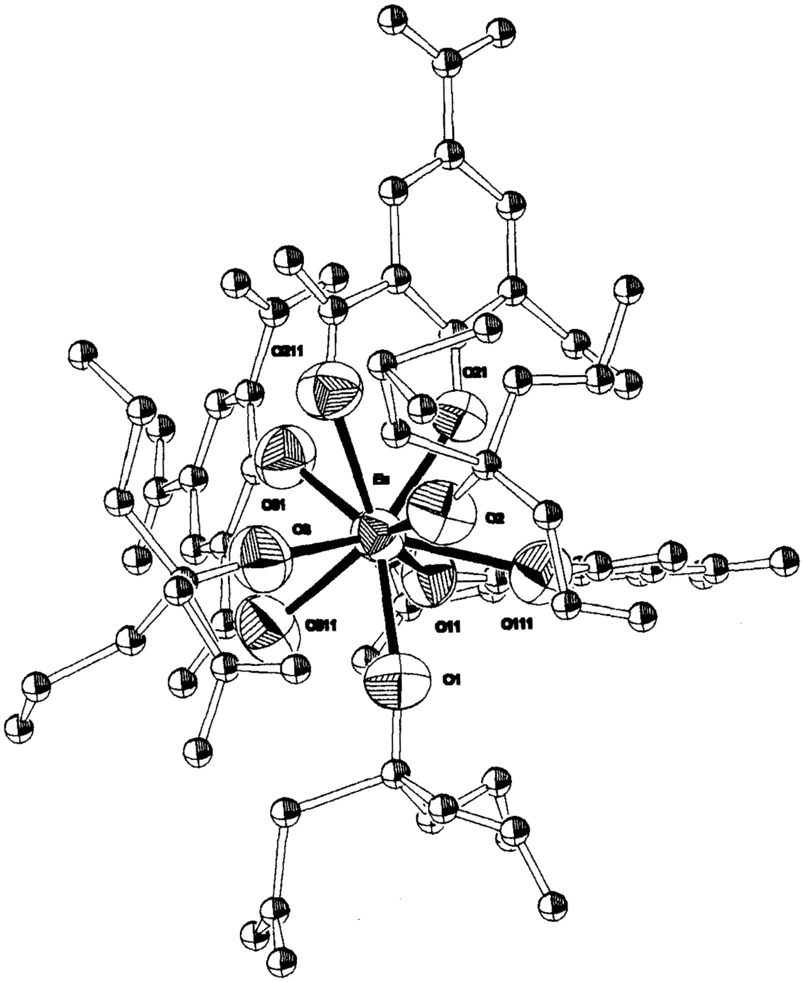

FIGURE 2 ZORTEP view of the complex Eu(pic)$_3$ · 3(DMVP). Thermal ellipsoids for Eu and O bonding atoms are drawn at 50% probability. For sake of clarity, other atoms are in an arbitrary scale.

Due to the rather poor diffraction quality of the crystals only the heavy atoms, the PO moieties and the pic groups were refined anisotropically. H-atoms were located on stereochemical grounds and refined riding on the atom they were attached to. In spite of this, the main purpose of the crystallographic work to determine the coordination polyhedra was achieved with experimental errors that allow comparison with structures of similar compounds.[15]

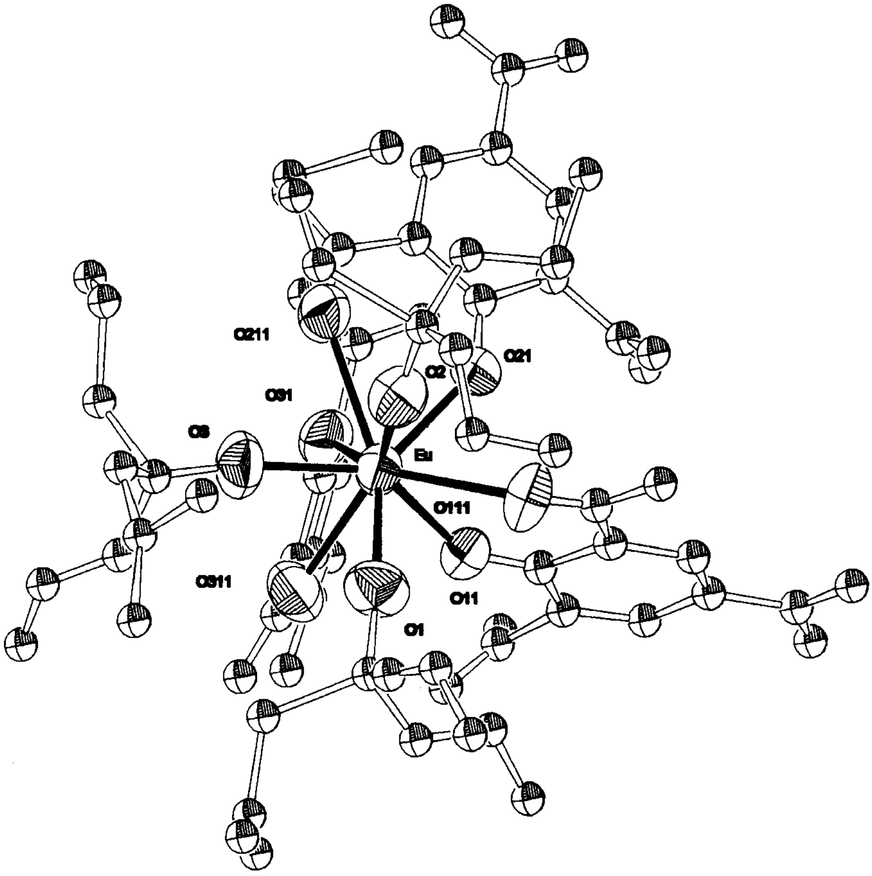

FIGURE 3 ZORTEP view of $Eu(pic)_3 \cdot 3(DEPP)$.

As can be seen in Table III and Figures 4 and 5, both coordination polyhedra are very similar and Eu distances and angles to the picrate groups are in good agreement, within experimental accuracy, with the values found in other complexes.[20] A non-coordinated water molecule was found in the DMVP complex.

The coordination polyhedra observed in this work are similar to most lanthanide picrate complexes, which are tricapped trigonal prisms, with one base formed by the oxygens of the neutral ligands. Observed dihedral angles are also similar, within experimental error, to the ones observed in similar compounds.[3,19,20]

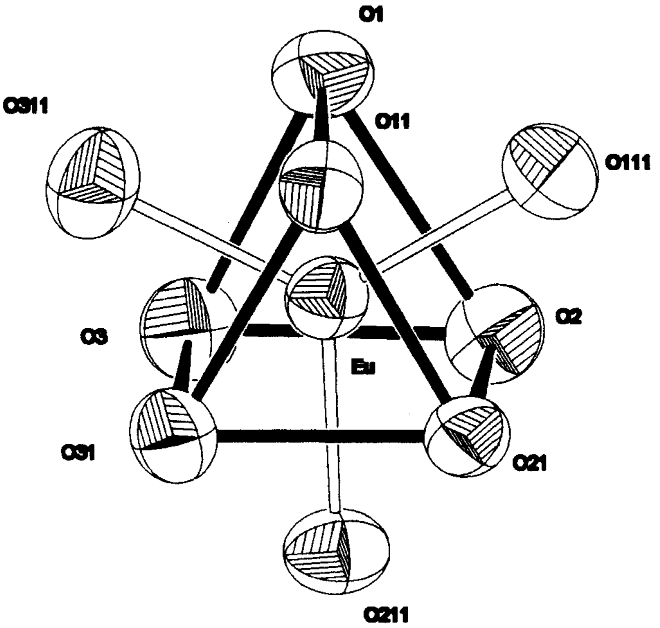

FIGURE 4 Coordination polyhedron of Eu(pic)$_3$ · 3(DMVP).

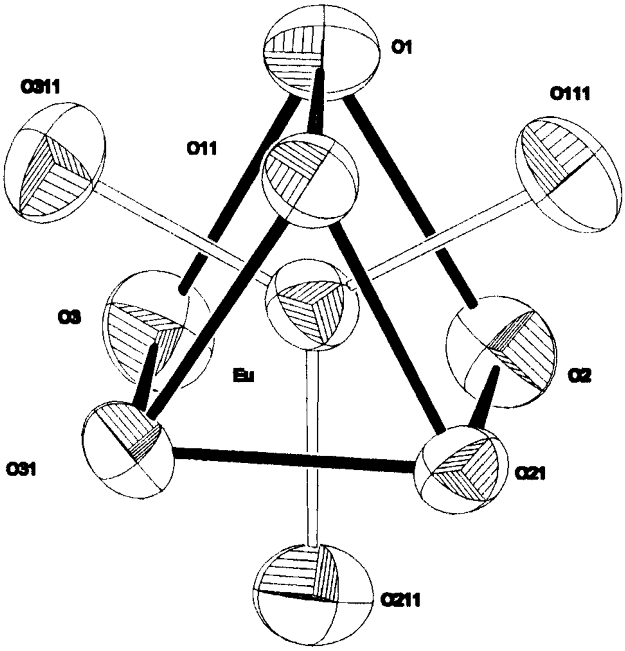

FIGURE 5 Coordination polyhedron of Eu(pic)$_3$ · 3(DEPP).

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