## COORDINATION COMPOUNDS

# Formation of Coordination Compounds in Gadolinium-Loaded Liquid Organic Scintillators (GdLS): Use of Mixed-Ligand Gadolinium Complexes in GdLS Preparation

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**Abstract**—The formation of coordination compounds between gadolinium 2-methylvalerate (Gd(2MVA)<sub>3</sub>) and trioctylphosphine oxide (TOPO) in a gadolinium-loaded liquid scintillator (GdLS) solution was studied by MALDI-TOF MS. The most abundant gadolinium-containing compound in the GdLS solution in the presence of TOPO is the monomer complex Gd(2MVA)<sub>3</sub> · (TOPO)<sub>2</sub>. In the absence of TOPO, the solution contains only Gd<sub>n</sub>(2MVA)<sub>3n</sub> (n = 2-5) association species. Therefore, TOPO prevents carboxylate polymerization in the solution and can be used as a stabilizer of the gadolinium compounds in GdLS. The existence of the Gd(2MVA)<sub>3</sub> · TOPO complex is confirmed by IR spectroscopy. The possibility of coordination between Gd(2MVA)<sub>3</sub> and 2,5-diphenyloxazole (PPO), the most common scintillation admixture, has been investigated. No complexes between Gd(2MVA)<sub>3</sub> and PPO have been detected by MALDI-TOF MS in the scintillator solution. IR spectroscopic data also do not provide any unambiguous indication of coordination between Gd(2MVA)<sub>3</sub> and PPO.

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Gadolinium-loaded liquid organic scintillators (GdLS) are widely used in many physical measurements involved in neutron detection. Particularly great interest in gadolinium-containing scintillators has been expressed in recent years because of the start of largescale experiments on the detection of neutrino flows from various sources, such as nuclear reactors and supernova outbursts. The reaction between a neutrino and a hydrogen atom of the organic solvent yields a neutron, which is then absorbed by a gadolinium nucleus. Since the efficiency of neutron absorption by the gadolinium nucleus is very high, the gadolinium concentration in the organic scintillator is usually ~0.1%. The problem of carrying out neutrino experiments includes the need for large amounts (tens of tons) of scintillator and taking measurements over a long time of several years. These two circumstances impose certain stability requirements on the scintillation properties of GdLS.

The stability of the scintillation properties of a scintillator means the constancy of the total amount of light collected by the photodetector. There are two possible factors in a decline in the light yield at a constant gadolinium concentration in the solution. The first is a decrease in the scintillation efficiency of the molecules containing aromatic rings, as well as the formation of new, "quenching" molecules capable of decreasing the efficiency of excitation transfer between solvent molecules. The second factor that can reduce the transparency of the solution in the emission spectral range is the possible formation of new compounds absorbing light in this range. In addition, gadolinium complexes can precipitate from the solution because of the decrease in their solubility caused by their hydrolysis or polymerization.

The purpose of this work was to evaluate only the effect of the processes involving gadolinium compounds and to study the complexes that these compounds can form in solutions of the organic scintillator upon prolonged use of the latter.

Scintillators based on gadolinium carboxylates or  $\beta$ -diketonates are being actively developed now for neutrino experiments [1–3]. There are only six gadolinium–ligand bonds in these compounds, although lan-

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thanides, including gadolinium, typically have a larger coordination number. Therefore, the gadolinium atom can form extra coordination bonds with electron donors present in the liquid organic scintillator. These donors can be oxazole-based scintillation admixtures containing the electron-donating elements oxygen and nitrogen, such as 2,5-diphenyloxazole (PPO). Furthermore, gadolinium carboxylates and  $\beta$ -diketonates can dimerize, and the formation of longer chains is not impossible.

In this study, the gadolinium compound was gadolinium 2-methylvalerate (Gd(2MVA)<sub>3</sub>), which is the most appropriate compound for GdLS preparation by extraction [1]. Solid Gd(2MVA)<sub>3</sub> was first synthesized. Its solubility and stability in the solution were enhanced by adding trioctylphosphine oxide (TOPO); Gd : TOPO = 1 : 3 mol/mol.

Here, we report coordination between  $Gd(2MVA)_3$ and PPO and between  $Gd(2MVA)_3$  and TOPO and the formation of dimer and polymer  $Gd(2MVA)_3$  association species in an organic scintillator solution based on a mixture of pseudocumene (20%) and dodecane.

The formation of  $Gd(2MVA)_3$  association species and  $Gd(2MVA)_3$  complexes with TOPO and PPO was investigated by matrix-assisted laser desorption ionization coupled with time-of-flight mass spectrometry (MALDI-TOF MS). The formation of coordination bonds between  $Gd(2MVA)_3$  and PPO and between  $Gd(2MVA)_3$  and TOPO was also studied by IR spectroscopy.

### **EXPERIMENTAL**

The starting chemicals were  $Gd_2O_3$  (99.9%) (REO), 2-methylvaleric acid (98%, Aldrich), PPO (chemically pure grade), TOPO (99%, Aldrich), hydrochloric acid (highpurity grade), aqueous ammonia (25%, highpurity grade), acetone (highpurity grade), pseudocumene (scintillation grade, P-357, Fischer Scientific Company), dodecane (highpurity grade), and benzene (highpurity grade).

2-Methylvaleric acid was purified by vacuum distillation; pseudocumene and dodecane, by passing them through alumina-packed columns.

**Gd(2MVA)**<sub>3</sub> **synthesis.** Gd(2MVA)<sub>3</sub> was synthesized using a modified lanthanide carboxylate synthesis procedure [4]. A dilute gadolinium chloride solution was added in drops to a vigorously stirred (900 rpm) solution of 2-methylvaleric acid neutralized with concentrated aqueous ammonia (gadolinium : acid = 1 : 3 mol/mol). The GdCl<sub>3</sub> solution was prepared by dissolving gadolinium oxide in concentrated hydrochloric acid and filtering out excess Gd<sub>2</sub>O<sub>3</sub>. The resulting precipitate was washed with deionized water to remove NH<sub>4</sub>Cl, with ethanol to remove excess 2-methylvaleric acid, and

with acetone to remove water. The resulting salt was dried at 110°C for 2 h.

The C, H, and Gd contents of the resulting  $Gd(2MVA)_3$  were determined by elemental microanalysis.

For Gd(2MVA)<sub>3</sub> anal. calcd. (%): C, 42.96; H, 6.56; Gd, 31.28. Found (%): C, 42.64; H, 6.59; Gd, 30.74.

 $Gd(2MVA)_3 \cdot 2PPO$  synthesis. PPO (2.83 g, 0.0128 mol) was added to absolute benzene (5 mL) to obtain a homogeneous solution. Next, dry gadolinium 2-methylvalerate (3.22 g, 0.0064 mol) was added in small portions under magnetic stirring. This yielded a viscous gel, which was stirred magnetically for 2 h. The product was poured into a Petri dish and was placed into a vacuum desiccator containing phosphorus(V) oxide. Benzene was collected in a liquid-nitrogen trap using a fore pump. The resulting complex was dried in the desiccator for 3 days.

 $Gd(2MVA)_3 \cdot TOPO$  synthesis. TOPO (1.2477 g) was added to hexane (10 mL), and  $Gd(2MVA)_3$  (1.6 g) was then added under stirring. The resulting complex with a small amount of hexane was placed into a vacuum desiccator and was dried over  $P_2O_5$  for 1 day. The complex remained liquid, viscous, and transparent like glass.

Subsequent studies demonstrated that this complex can be obtained in a simpler way by combining appropriate amounts of Gd(2MVA)<sub>3</sub> and TOPO powders.

**IR spectra** were recorded as KBr pellets on a Specord UR 75 spectrophotometer.

**MALDI-TOF MS experiments** were carried out on an Ultraflex TOF/TOF mass spectrometer (Bruker) using an  $N_2$  laser (wavelength of 337 nm). Mass spectra were recorded in the positive ion mode at an accelerating voltage of 25 kV. The matrix was anthracene.

**X-ray diffraction studies** demonstrated that all of the synthesized compounds are X-ray-amorphous.

## **RESULTS AND DISCUSSION**

Lanthanide carboxylates and  $\beta$ -diketonates are prone to polymerization, which can occur both in solution and in the solid phase, as is indicated by the decrease in their solubility in the course of time [5–7]. (As was demonstrated for anhydrous lanthanide acetylacetonates [5] and nickel acetylacetonates [8], their polymerization is due to the sharing of oxygen atoms of the  $\beta$ -diketone. The polymerization of the carboxylates is due to the COO<sup>-</sup> groups functioning as bridging ligands [9].)

This polymerization can be hampered by using gadolinium compounds with bulkier ligands (e.g., gadolinium dipivaloylmethanate or pivalate) in the scintillator



Fig. 1. IR spectrum of PPO.

cocktail. However, even in this case, polymerization cannot be suppressed completely [10, 11].

In addition, because of the large coordination numbers typical of the gadolinium atoms, the synthesis of gadolinium compounds in aqueous solutions yields complexes containing water molecules in their inner coordination sphere [11, 12]. When drying these complexes, it is practically impossible to prevent hydrolysis completely.

None of the drying methods tested by Pope et al. [13]—room-temperature drying over MgClO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub>, or CaCl<sub>2</sub> and isothermal dehydration—afforded an anhydrous acetylacetonate. Hydroxo complexes were present in all cases. Furthermore, it is likely that the formation of hydroxo complexes always takes place when hydrated  $\beta$ -diketonates are dissolved in organic solvents (benzene, ethanol, methanol, etc.) [13]. Particularly rapid hydrolysis is observed as the solution is heated. The hydroxo complexes forming in the solution polymerize, yielding hydroxo polymers.

In our opinion, in order to avoid both the polymerization and hydrolysis of the gadolinium complexes, it is necessary to introduce, into these complexes, a compound that can replace water molecules and completely saturate the coordination sphere without being favorable for polymerization.

It is well known that the coordinatively unsaturated  $\beta$ -diketonates and carboxylates of paramagnetic lanthanide ions can add Lewis base molecules. Particular attention has been focused on the synthetic conditions, structure, and properties of lanthanide  $\beta$ -diketonate adducts. The Lewis bases that have been used in the adducts are alkyl phosphates (tributyl phosphate, TBP) [14, 15], phosphine oxides (trioctylphosphine oxide, TOPO [11, 14]; triphenylphosphine oxide, TPPO [14, 16]), 1,1'-dipyridyl (Dipy) [14, 17, 18], 1,10-phenan-throline (Phen) [14, 17], and dimethyl sulfoxide [19].

There have been similar studies aimed at the synthesis and characterization of lanthanide carboxylate adducts. The compounds that have been used as extra ligands are pivalic acid [9], 1,10-Phen [9], TPPO [20, 21], and TOPO [21].

There is some probability that 2,5-diphenyloxazole, which is commonly used as a scintillation admixture in GdLS, cal also form coordination bonds with gadolinium carboxylates through the oxygen and nitrogen heteroatoms of its oxazole ring. However, IR spectroscopic data (Figs. 1-3) provide no unambiguous indication that these coordination bonds exist in the  $GdR_3$ . 2PPO adduct, because the characteristic bands of the phenyl radicals of PPO (Fig. 1; v(C-C(arom)) =1609.07, 1587.48, 1543.40, 1480.95, and 1445.47 cm<sup>-1</sup>) are overlapped with the characteristic bands of the carboxylate groups of Gd(2MVA)<sub>3</sub> (Fig. 2). (The IR spectrum of the starting metal salt (Fig. 2) shows carboxyl bands at 1533.42 cm<sup>-1</sup> ( $v_{as}$ (COO)) and 1423.52 cm<sup>-1</sup>  $(v_s(COO))$ , indicating that the carboxyl group is coordinated in a bidentate bridging mode. In the IR spectrum



Fig. 2. IR spectrum of Gd(2MVA)<sub>3</sub>.

of the adduct, the vibration frequencies of the carboxyl groups are the same (1533.25 and 1422.15 cm<sup>-1</sup>) and the bands at 1585.24 and 1443.59 cm<sup>-1</sup> are likely due to the phenyl radicals of PPO.) The characteristic bands were identified using reference data [22, 23].

The spectrum of the initial salt (Gd(2MVA)<sub>3</sub>) has a broad band at 3417 cm<sup>-1</sup> (v(OH)), suggesting that the initial carboxylate contains water molecules. It follows from the elemental analysis data that the water content of the initial salt does not exceed 0.2 wt %. In the IR spectrum of the GdR<sub>3</sub> · 2PPO adduct, the OH stretching band is missing. However, this is not an unambiguous indication that PPO molecules coordinate to the initial salt, replacing the water molecules. It is possible that the residual water leave the salt during GdR<sub>3</sub> · 2PPO synthesis upon the evaporation of the absolute benzene used as the solvent.

Our MALDI-TOF MS data do not indicate the existence of stable complexes between  $Gd(2MVA)_3$  and PPO, but they demonstrate the presence of carboxylate oligomers in the solution of  $(Gd(2MVA)_3) \cdot 2PPO$  in pseudocumene. (The applicability of the MALDI-TOF MS method to the identification of lanthanide carboxylate association species in solutions was demonstrated in [20, 21].)

Figure 4 shows the mass spectrum of a  $GdR_3 \cdot 2PPO$  solution in pseudocumene ( $c_{Gd} = 1$  g/L) with an anthracene matrix. (Note that gadolinium has six stable

isotopes, so the mass spectrum of any gadolinium-containing complex has a distinctive profile. This makes it possible to identify the complex in the total mass spectrum of GdLS. An example of an isotopic multiplet is shown in Fig. 5.)

**Table 1.** Assignment of signals from Gd-containing complexesin the MALDI-TOF mass spectrum of  $Gd(2MVA)_3 \cdot 2PPO$ in pseudocumene (anthracene matrix)

Assignment (strongest peak)	m/z.		Relative
	observed	calculated	intensity, %
$[Gd_2(2MVA)_5]^+$	891.3546	891.2288	100
$[Gd_3(2MVA)_8]^+$	1394.3662	1393.3810	64.5
$[Gd_4(2MVA)_{11}]^+$	1896.4895	1895.5328	27.2
$[Gd_5(2MVA)_{14}]^+$	2398.6130	2397.6846	13.0



Fig. 3. IR spectrum of  $Gd(2MVA)_3 \cdot 2PPO$ .

Table 2 presents the assignment of the main peaks from gadolinium complexes in the pseudocumene solution. (The masses refer to the strongest peaks of the iso-



Fig. 4. MALDI-TOF mass spectrum of a solution of  $Gd(2MVA)_3 \cdot 2PPO$  in pseudocumene (anthracene matrix).

topic multiplets and were calculated using the Isotope Pattern program.)

It is clear from Table 1 that gadolinium 2-methylvalerate in the solution exists mainly as dimers (100%) and association species containing three gadolinium atoms (64.5%), four ones (27.2%), or five ones (13.0%).

We suggested use of TOPO in order to prevent carboxylate polymerization in the scintillator solution, and we synthesized and characterized the  $Gd(2MVA)_3 \cdot TOPO$  adduct.

The IR spectrum of the  $Gd(2MVA)_3 \cdot TOPO$  complex (Fig. 6) indicates that the extra ligand is likely in the inner coordination sphere. The characteristic absorption band v(P=O) of the ligand (1135 cm<sup>-1</sup>) is shifted to lower frequencies relative to the same band of free TOPO (1160 cm<sup>-1</sup>) [14]. The spectrum of the complex does not show any v(OH) absorption band in the 3000–3600 cm<sup>-1</sup> range, indicating that the complex is completely dehydrated. In addition, the spectrum of  $Gd(2MVA)_3 \cdot TOPO$  exhibits a band due to the free carboxylic acid (1710.36 cm<sup>-1</sup>), which is evidence that the extra ligand TOPO partially replaces the acid anion in the carboxylate molecule.

The complexes between  $Gd(2MVA)_3$  and TOPO in the scintillator solution were also studied by MALDI-TOF MS.

We chose to examine a scintillator containing gadolinium 2-methylvalerate (1 g/L in terms of Gd), scintil-



**Fig. 5.** MALDI-TOF mass spectrum of the gadolinium-containing scintillator. Scintillator composition:  $Gd(2MVA_3) + PPO (3 g/L) + bis-MSB (30 mg/L)$ . Solvent: pseudocumene (20%) + dodecane. The scintillator storage time before recording the spectrum was 1 year. The matrix is anthracene.

lation admixtures (PPO, 2 g/L; bis-MSB, 30 mg/L), and TOPO as the stabilizing agent (Gd : TOPO = 1 : 3 mol/mol). The solvent was a mixture of pseudocumene (20%) with dodecane, which has a high flash point and is compatible with acryl, a constructional material used in large-volume scintillators. Before experiments, the scintillator was stored for about 1 year. (Figure 5 shows the MALDI-TOF mass spectrum of this scintillator with an anthracene matrix.)

Figure 7 displays the mass spectrum of the  $[Gd(2MVA)_2(TOPO)_2]^+$  complex as an example of gadolinium clusters. Table 2 lists the observed and calculated masses for the peaks from all isotopes of this complex. Mass calculations were carried out using the Isotope Pattern program.

Table 3 presents the assignment of the main peaks from the gadolinium-containing complexes in the scintillator solution. (The masses refer to the strongest peaks of the gadolinium clusters.) It is clear from Table 3 that, in the presence of TOPO, most of the gadolinium is in the form of a carboxylate monomer containing two TOPO molecules ([Gd(2MVA)<sub>2</sub>(TOPO)<sub>2</sub>]<sup>+</sup>).

Thus, TOPO hampers carboxylate polymerization in the scintillator solution, thereby stabilizing the scintillator.

In our opinion, it is appropriate to presynthesize a gadolinium adduct with TOPO or another extra ligand for saturating the coordination sphere of the gadolin-

Table 2. Mass spectrum	of $[Gd(2MVA)_2(TOPO)_2]^+$
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Observed	Relative intensity, %	Calculated	Relative intensity, %
1156.4584	10.27	1156.8077	5.455
1157.4922	43.50	1157.8095	39.853
1158.4989	79.88	1158.8102	75.539
1159.5018	80.360	1159.8120	80.385
1160.5089	100	1160.8124	100
1161.5121	53.735	1161.8151	52.480
1162.5151	70.085	1162.8148	70.266
1163.5171	43.441	1163.8176	39.475
1164.4960	22.166	1164.8207	13.024
1164.9504	3.383	1165.8238	3.050



**Fig. 6.** IR spectrum of  $Gd(2MVA)_3 \cdot TOPO$ .



Fig. 7. MALDI-TOF mass spectrum of [Gd(2MVA)<sub>2</sub>(TOPO)<sub>2</sub>]<sup>+</sup>.

ium atom and to introduce this adduct into the scintillator solution.

The gadolinium adduct should be prepared immediately after the synthesis of a gadolinium carboxylate in order to avoid hydrolysis and carboxylate polymerization. The advantage offered by the mixed-ligand gadolinium complexes in the preparation of liquid scintillators is that these complexes are coordinatively saturated compounds readily soluble in organic solvents and resist hydrolysis and polymerization when stored as a pure substance or in a scintillator solution.

Table 3. Assignment of signals from Gd-containing complexes in the MALDI-TOF mass spect	rum of the GdLS solution
(Gd(2MVA) <sub>3</sub> + 3TOPO + 1.4PPO + 0.02bis-MSB; anthracene matrix; scintillator storage time of	1 year)

Assignment (strongest peak)	mlz		Pelative intensity %
	observed	calculated	Relative intensity, 70
[Gd(2MVA) <sub>2</sub> TOPO] <sup>+</sup>	773.8613	774.4440	7.6
$[Gd(2MVA)_2(TOPO)_2]^+$	1160.5089	1160.8114	100
$[Gd_2(2MVA)_5 (TOPO)]^+$	1277.4779	1277.5955	11.7
$[Gd(2MVA)_2(TOPO)_3]^+$	1547.0785	1547.1792	3.7
[Gd <sub>2</sub> (2MVA) <sub>5</sub> (TOPO) <sub>2</sub> ] <sup>+</sup>	1664.0220	1663.9632	18.0

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