Ternary Lanthanide Complexes of the Type $M(Hsal)_3(TPX\rightarrow O)_2$ and a Fluorescence Spectral Study of the Eu(III) Analogue

SHYAMA P. SINHA

Department of Inorganic Chemistry, The University, Leeds 2, England

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Ternary lanthanide complexes of the general formula $M(Hsal)_3(TPX \rightarrow O)_2$, where M=lanthanide(III) ion, Hsal=salicylate ion=$C_6H_4(OH)COO^-$ and X=P or As have been isolated as solids from the benzene phase during liquid-liquid extraction studies of $M(Hsal)_3$ complexes with benzene solutions of TPX → O. The coordinated nature of the TPXO ligands has been established from the observed shifts of the X → O frequency in the infrared. A lowering of the 1190 cm^{-1} P → O frequency where X=P, and an increase in the 885 cm^{-1} As → O frequency where X=As have been observed for the ternary complexes. The infrared spectra of the ternary complexes in general indicate the coordinated nature of the salicylate ions.

The luminescence spectra of $Eu(Hsal)_3(TPPO)_2$ and $Eu(Hsal)_3(TPAsO)_2$ complexes have also been investigated at 77 °K. Beside the emission of the characteristic red europium fluorescence due to the excitation of the complexes with near UV light, emission of a blue molecular phosphorescence from the complexes has also been observed. The fluorescence intensities of the f → f transitions are, however, weak. This point has been discussed.

In 1942 WEISSMAN[1] demonstrated intramolecular energy transfer from coordinated salicylate ligand moiety to the central Eu(III) ion causing characteristic red fluorescence. Our interest in europium(III)-salicylate stems from a study of formation constants of the species by a solvent extraction method[2]. It is found that non-polar solvents like benzene is incapable of extracting Eu(III)-salicylate to any extent, whereas extraction occurs when polar solvents like higher alcohols are used. It has also been found that adducts of Eu(III)-salicylate can be extracted synergically into benzene containing a neutral oxygen donor ligand from an aqueous solution of Eu(III)-salicylate. Donor ligands such as tributyl phosphate (TBP), triphenylphosphine oxide (TPPO) and triphenylarsine oxide (TPAsO) are found[3] to be coordinated to the formally neutral europium(III)-tris-salicylate complex.

$$M(Hsal)_{3\,\mathrm{aqu}} + L_{\mathrm{org}} \rightarrow [M(Hsal)_3L_2]_{\mathrm{org}}$$

M = trivalent lanthanide, Hsal = uninegative salicylate ion = $C_6H_4(OH)COO^-$, L = TBP, TPPO, TPAsO.

During these extraction experiments, it was possible to isolate solid crystalline ternary complexes of the type $M(Hsal)_3L_2$ where L = TPPO and TPAsO from the benzene layer. Complexes where L = TBP were liquid. For the purpose of spectroscopic investigation we have prepared Eu(III) and Nd(III) complexes. In a typical preparation of the complexes, usually an aqueous solution of either the chloride or nitrate salt of the lanthanide (1 mmole in 10 ml water) was first treated with an aqueous solution of sodium salicylate (3 m mole in 10 ml) and the mixture was then extracted with a benzene solution of the neutral ligand, TPPO or TPAsO (2 m mole in 60 ml). The benzene layer was then separated, washed twice with small portion of water and allowed to evaporate slowly at room temperature giving well formed crystalline complexes. These were washed a few times with small volumes of benzene and dried in a vacuum desiccator.

$Nd(C_6H_4(OH)COO)_3((C_6H_5)_3PO)_2$

calc.	C 62.66,	H 4.12;
found	C 64.3,	H 4.3;

$Nd(C_6H_4(OH)COO)_3((C_6H_5)_3AsO)_2$:

calc.	C 58.01	H 3.81;
found	C 58.5,	H 4.0;

$Eu(C_6H_4(OH)COO)_3((C_6H_5)_3PO)_2$:

calc.	C 62.24,	H 4.09;
found	C 63.8,	H 4.4;

$Eu(C_6H_4(OH)CCO)_3((C_6H_5)_3AsO)_2$:

calc.	C 57.62,	H 3.79;
found	C 58.5,	H 4.0.

The coordinated nature of the neutral ligands (TPPO, TPAsO) has been established from a study of the infrared spectra of the complexes.

Reprints request to Dr. S. P. SINHA, Dept. of Inorganic Chemistry, University of Leeds, *Leeds LS2 9JT*, England.

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Infrared Spectra of the Ternary $M(Hsal)_3(TPX \rightarrow O)_2$ Complexes

The infrared peaks of the ternary $M(Hsal)_3(TPX \rightarrow O)_2$ complexes [M(III) = Nd, Eu; X = P, As] are tabulated and compared with TPPO and TPAsO in Table 1. The ternary complexes show complicated infrared spectra due to the presence of coordinated salicylate ion $[C_6H_4(OH)COO^-]$ and coordinated TPX → O peaks. The shift of 1190 cm^{-1} P → O stretching vibration in $M(Hsal)_3(TPPO)_2$ complexes and that of the 885 cm^{-1} As → O stretching vibration in $M(Hsal)_3(TPAsO)_2$ complexes due to coordination of the X → O groups are shown in Figs. 1 and 2.

A shift $(\nu_{max}^{comp} - \nu_{max}^{TPXO})$ of some $20 - 30$ cm^{-1} of the P → O stretching vibration towards lower wavenumber has been observed (Table 2) for the ternary lanthanide complexes, $M(Hsal)_3(TPPO)_2$. Such decrease in P → O stretching frequency is invariably observed in the complexes containing coordinated TPPO. The 3d-transition metal complexes show[4] a negative shift of $40 - 70$ cm^{-1}. The decrease in P → O stretching frequency is usually attributed[4–6] to a decrease in or lack of $p\pi - d\pi$ bonding within the PO group. The coordination of TPPO via oxygen of the P → O group tends to enhance the σ-bond character of the PO group while the strength of $p\pi - d\pi$ bonding is decreased. The effect of enhancement of the σ character should be reflected as (i) an increase in P → O fundamental frequency while (ii) a decrease in P → O fundamental frequency is expected due to concomitant decrease in $p\pi - d\pi$ bonding. Hence, the two effects are acting

TPPO	3060 (w)	1590 (m)	1488 (m)	1440 (s)	1395 (w)	
	1332 (w)	1312 (m)	1275 (w)	1190 (s)	1155 (sh)	
	1122 (s)	1095 (sh)	1072 (m)	1028 (w)	998 (m)	
	925 (w)	862 (m)	850 (m)	758 (s)	750	727 (s)
	700 (s)	540 (s)	510 (m)	460 (w)	448 (w)	292 (s)
$Nd(Hsal)_3(TPPO)_2$	3060 (w)	1625 (m)	1590 (s)	1570 (m)	1485 (s)	
	1462 (s)	1440 (s)	1405 (sh)	1390 (s)	1362 (s)	
	1340 (sh)	1308 (w)	1255 (s)	1225 (w)	1190 (sh)	
	1172 (s)	1140 (w)	1126 (s)	1098 (m)	1075 (w)	
	1030 (m)	1000 (w)	870 (s)	820 (s)	764 (s)	
	755 (s)	728 (s)	698 (s)	670 (m)	542 (s)	455 (w)
	390 (m)					
$Eu(Hsal)_3(TPPO)_2$	3060 (w)	1625 (m)	1595 (s)	1560 (m)	1485 (s)	
	1462 (s)	1438 (s)	1405 (sh)	1390 (s)	1360 (s)	
	1310 (w)	1255 (s)	1225 (w)	1185 (sh)	1160 (s)	
	1122 (s)	1092 (m)	1072 (w)	1030 (m)	1000 (w)	
	870 (s)	820 (s)	760 (s)	750 (sh)	725 (s)	695 (s)
	670 (m)	542 (s)	460 (w)	398 (m)	300 (sh)	
TPAsO	1485 (m)	1440 (s)	1318 (w)	1185 (w)	1160 (vw)	
	1090 (s)	1070 (vw)	1028 (w)	1000 (m)	935 (w)	
	885 (s)	855 (w)	762 (s)	745 (s)	700 (sh)	692 (s)
	682 (m)	484 (s)	478 (s)	460 (s)	370 (s)	355 (s)
$Nd(Hsal)_3(TPAsO)_2$	1625 (m)	1595 (s)	1570 (s)	1485 (s)	1464 (s)	
	1430 (s)	1390 (s)	1360 (s)	1310 (m)	1255 (s)	
	1225 (w)	1185 (w)	1158 (w)	1142 (m)	1090 (s)	
	1070 (w)	1030 (m)	1000 (m)	900 (s)	870 (s)	820 (s)
	760 (s)	740 (s)	708 (s)	692 (s)	670 (s)	538 (w)
	480 (s)	460 (m)	392 (m)	365 (s)		
$Eu(Hsal)_3(TPAsO)_2$	1625 (m)	1598 (s)	1570 (s)	1485 (s)	1462 (s)	
	1440 (s)	1392 (s)	1362 (s)	1310 (m)	1255 (s)	
	1225 (w)	1185 (w)	1160 (w)	1142 (m)	1090 (s)	
	1030 (m)	1000 (m)	905 (s)	870 (s)	820 (m)	762 (s)
	742 (s)	708 (m)	692 (s)	672 (m)	538 (w)	480 (s)
	460 (m)	395 (m)	365 (s)			

w = weak, m = medium, s = strong, sh = shoulder.

Table 1. Infrared peaks (in wavenumber) of TPPO, $M(Hsal)_3(TPPO)_2$, TPAsO and $M(Hsal)_3(TPAsO)_2$.

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	X → 0 stretching (cm−1)	$\nu_{\max}^{\text{comp}} - \nu_{\max}^{\text{TPXO}}$ (cm−1)
TPPO	1190 (s)	—
Nd(III)-complex	(1190), 1172 (s)	−18
Eu(III)-complex	(1190), 1160 (s)	−30
TPAsO	885 (s)	—
Nd(III)-complex	900 (s)	+15
Eu(III)-complex	905 (s)	+20

Values in parenthesis are weak shoulders; s=strong.

Table 2. The shift of P → O and As → O stretching vibrations in $M(Hsal)_3(TPPO)_2$ and $M(Hsal)_3(TPAsO)_2$ complexes.

opposite to each other. However, a net lowering of the 1190 cm^{-1} P → O fundamental in the complexes definitely indicates that the later effect (factor ii) predominates over the former (factor i).

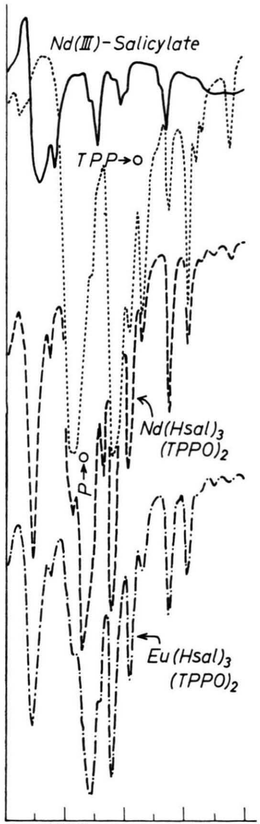

Fig. 1.

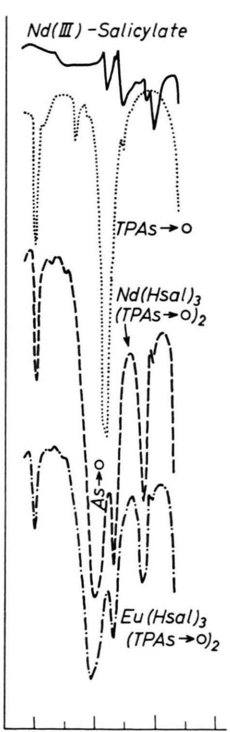

Fig. 2.

Fig. 1. Comparison of the infrared spectra of TPPO, $M(Hsal)_3(TPPO)_2$ and $Nd(Hsal)_3$ (as a representative of lanthanide salicylate) in the P → O stretching region.

Fig. 2. Comparison of the infrared spectra of TPAsO, $M(Hsal)_3(TPAsO)_2$ and $Nd(Hsal)_3$ (as a representative of lanthanide salicylate) in the As → O stretching region.

A strong band at 885 cm^{-1} is observed for TPAsO (Table 1) and is assigned to the As → O stretching vibration. This values agrees with an average value of 890 cm^{-1} for As → O vibration obtained in an investigation of a large number of trialkylarsine oxides[7]. The frequency shift, $\nu_{\max}^{\text{comp}} - \nu_{\max}^{\text{TPAsO}}$, of the As → O stretching vibration in the complexes containing TPAsO is not very clear cut. Complexes such as $Cu(TPAsO)_2Cl_2$, $Cu(TPAsO)_2Br_2$ and $Hg(TPAsO)_4(ClO_4)_2$ show a decrease[5, 8, 9] in As → O stretching frequency, while an increase[6] by some 20 – 30 cm^{-1} is observed in other complexes, $Mn(TPAsO)_2Cl_2$, $Mn(TPAsO)_2 \cdot Br_2$. In the present case of the ternary $M(Hsal)_3(TPAsO)_2$ [M(III) = lanthanide] complexes a strong, slightly broadened peak around 900 cm^{-1}, with a sharp but less intense peak at 870 cm^{-1} (Fig. 2, Table 2) is observed. Taking into account that the $M(Hsal)_3$ type lanthanide(III) complexes are transparent in the region between 1035 and 885 cm^{-1} (Fig. 2) we can assign the peak around 900 cm^{-1} as due to the coordinated As → O group. No unambiguous assignment of the 870 cm^{-1} peak could, however, be made as this peak may have some contribution from the absorption of $M(Hsal)_3$ in the 885 – 820 cm^{-1} region (Fig. 2). It might be mentioned here that a splitting of the As → O fundamental frequency has also been observed[6] in some complexes. Taking the band around 900 cm^{-1} in the ternary $M(Hsal)_3(TPAsO)_2$ complexes as due to the coordinated As → O group we arive a value of about 15 – 20 cm^{-1} for $\nu_{\text{map}}^{\text{comp}} - \nu_{\max}^{\text{TPAsO}}$. The positive quantities (Table 2) indicate an increase in As → O frequency due to coordination in the case of our ternary complexes. Assuming that P → O and As → O groups have relatively low π-accepting capacity we would have expected the same sort of behaviour of the As → O frequency shift as in the ternary $M(Hsal)_3(TPPO)_2$ complexes if factor (ii) was predominating. The cause for the increase in As → O frequency in these ternary complexes and in the above mentioned Mn(II)-complexes is still uncertain.

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In the case of lanthanide salicylates the following important changes have been observed (unpublished results of the author).

(i) occurance of peak around 1620 cm^{-1};

(ii) new peak around 1550 cm^{-1};

(iii) splitting of 1380 cm^{-1} sodium salicylate peak into two peaks at ~ 1420 and 1390 cm^{-1} in the lanthanide salicylates;

(iv) a considerable decrease in intensity of the peak around 1300 cm^{-1};

(v) the absence of 985 cm^{-1} sodium salicylate peak in the complexes.

Although due to the complicated nature of the infrared spectra of the ternary $M(Hsal)_3(TPX \rightarrow O)_2$ complexes, a complete and unambiguous assignment of all salicylate peaks is impossible, the ternary complexes in general show the changes mentioned above. In particular the absence of a strong 980 cm^{-1} peak is indicative of the coordinated nature of all salicylate ligands.

There can hardly be any doubt that the peaks of the ternary complexes in the $\sim 1590-1560$ cm^{-1} region (Table 1) are due to the antisymmetric OCO stretching vibration and the strong peak at ~ 1390 is due to the symmetric OCO stretching vibration of the coordinated salicylate ions. The following separations between the antisymmetric and symmetric OCO vibrations have been observed:

sodium salicylate ~ 200 cm^{-1},
lanthanide salicylate $\sim 190-200$ cm^{-1},
ternary $M(Hsal)_3(TPX \rightarrow O)_2 \sim 200$ cm^{-1}.

Tentatively the peak around 670 cm^{-1} in the ternary complexes is assigned to the symmetric OCO bending vibration and the band around 390 cm^{-1} to the OCO rocking vibration of the salicylate groups. From the solvent extraction studies [2, 3] and the infrared evidences we conclude that all three salicylate ligand moieties and the two TPX → O groups are coordinated to the central lanthanide ion, giving a coordination number of eight: $3 \times 2 = 6$ oxygens from salicylate ions ($C_6H_4 <^{OH}_{COO^-}$) and $2 \times 1 = 2$ oxygens from the neutral ligands. Coordination numbers higher than six is not unusual for the trivalent lanthanides [10].

Fluorescence Spectra of $Eu(Hsal)_3(TPPO)_2$ and $Eu(Hsal)_3(TPAsO)_2$ Complexes

The fluorescence spectra of the above two complexes were measured in the solid state at 77 °K. The results are tabulated in Table 3. Usually, the Eu(III)-complexes show [10] sharp fluorescence lines due to the intra f – f transitions ($^5D_J \rightarrow {}^7F_J$). Increase in fluorescence intensity has been achieved by substituting the parent ligand with proper groups, replacement of the ligand by a better coordinating agent or by using synergic agents [10]. Hence, it was thought that by introducing the neutral TPX → O donors to the formally uncharged Eu(III)-salicylate, an increase in fluorescence intensity would result. It is, however, clear from Table 3 that the overall fluorescence intensity for both complexes is very low although $Eu(Hsal)_3(TPAsO)_2$ complex shows relatively stronger fluorescence with respect to $Eu(Hsal)_3(TPPO)_2$ complex. This is somewhat unexpected, because substitution of bulkier ligands that absorb more energy would ordinarily increase the pump power in comparison with smaller ligands and hence an increase in Eu(III) fluorescence intensity. A similar situation has been observed by NEHRICH et al. [11] who found that Eu(III)-trifluoroacetylacetonate prepared from piperidine medium has low fluorescence intensity for $^5D_0 \rightarrow {}^7F_2$ transition and does not lase, whereas the same complex when prepared from ammonia showed laser action.

Transitions	wavelength Å (in air)	wavenumber cm^{-1} (in vacuum)	Relative intensity
$Eu(Hsal)_3(TPPO)_2$			
$^5D_0 \rightarrow {}^7F_0$	5797	17 250	0.4
$^5D_0 \rightarrow {}^7F_1$	5909	16 920	0.95
	5927	16 870	1.2
	5943	16 830	0.89
$^5D_0 \rightarrow {}^7F_2$	6126	16 320	3.5
	6172	16 200	6.5
$Eu(Hsal)_3(TPAsO)_2$			
$^5D_0 \rightarrow {}^7F_0$	5797	17 250	0.54
$^5D_0 \rightarrow {}^7F_1$	5903	16 940	2.6
	5921	16 890	2.66
	5947	16 820	2.2
$^5D_0 \rightarrow {}^7F_2$	6117	16 350	7.8
	6142	16 280	13.2
	6167	16 220	20.0

Table 3. Details of the fluorescence spectra of the ternary Eu(III)-complexes at 77 °K.

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It might also be mentioned here that the fluorescence intensities of these complexes are very much lower than the other known eight coordinated Eu(III) complexes[12, 13].

Beside the weak f – f fluorescence both ternary complexes showed relatively strong bluish molecular phosphorescence. Earlier both line emission and molecular phosphorescence has been observed[14–16] for some β-diketonate complexes of Eu(III). In the case of β-diketonate complexes it was assumed that the observed phosphorescence originated from the same species in which the intramolecular energy transfer is taking place. However, as the experiments with Eu(III)-β-diketonates were carried out in frozen solutions, the possibilty of dissociation of the complex could not be excluded. Indeed, BHAUMIK et al.[17] were able to show that the spectrum profile of the phosphorescence emisson from the frozen solution of the chelates was identical with that of the free ligand. Hence, it is proposed that in solution some dissociation of the chelated species takes place giving rise to a reasonable amount of the non-coordinated ligand. In the present case of the ternary complexes where the red line emission and blue phosphorescence were observed in the solid state, the question for dissociative species does not arise and it could be safely argued that the molecular phosphorescence is originating from the triplet state of the coordinated ligand.

Without having further knowledge of the phosphorescence and red fluorescnece lifetimes of the complexes, both in the solid state and in solution, it would be premature to comment on the mode of energy transfer and the nature of the triplet state in the complexes. Such studies is planned for the near future.

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