Heterobimetallic *d*−*f* Metal Complexes as Potential Single-Source Precursors for MOCVD: Structure and Thermodynamic Study of the Sublimation of [Ni(salen)Ln(hfa)$_3$], Ln = Y, Gd

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Received March 30, 1998

Keywords: Heterobimetallic complexes / Lanthanides / Nickel / Mass spectrometry / Thermochemistry

Heterobimetallic [Ni(salen)Ln(hfa)$_3$] species [H$_2$salen and Hhfa being *N,N′*-ethylenebis(salicylideneimine) and hexafluoroacetylacetone respectively], where Ni(salen) acts as a neutral chelating ligand towards Ln^{III}, form a series of isostructural compounds for Ln = Y^{III} and any lanthanide^{III} cation from La to Yb. They are also isostructural with some of the [Cu(salen)Ln(hfa)$_3$] compounds. They sublime without decomposition under vacuum which makes them potential single-source precursors in MOCVD. Sublimation, thermal behaviour, pressure and composition of the vapour phase versus temperature have been studied for the yttrium derivative, by means of thermal analyses, and mass spectrometry using a Knudsen cell. The dissociation process [Ni(salen)Y(hfa)$_3$] = Ni(salen) + Y(hfa)$_3$ has been thermodynamically investigated. Information on the solid-state intermolecular interactions in relation with volatility was obtained through the crystal structure determination of the gadolinium derivative. A comparative structural study of [Ni(salen)Gd(hfa)$_3$] and [Cu(saloph)Y(hfa)$_3$], [H$_2$saloph is *N,N′*-*o*-phenylenebis(salicylideneimine)], allows to understand why the latter is less volatile than the former despite similar molecular and solid-state structures.

Introduction

Many materials for high technology applications are heterometallic compounds in which at least two different metal elements are associated ($BaTiO_3$, $NaNbO_3$, $YBa_2Cu_3O_7$, AsGa, NiAl, ...). Their preparation as thin films using the technique of CVD requires as much precursors as metal elements to deposit. The idea of using single-source precursors is somewhat attractive since it allows a simplification of the reactor design and processing conditions, and a good control of the gas phase composition up to the deposition zone[1]. It has initiated a quest for volatile heterometallic compounds which is by itself a chemical challenge. Pioneering works include the growth of AsGa films from compounds such as $R_3As-GaR'_3$[2]. More recently, intermetallic films associating a p^3 element (Ga, In) and a *d* element (Ni, Co, Pt) have been grown from complexes with non-bridged[3][4][5] or bridged[6][7] $d-p^3$ bond. This approach was boosted up when the technique of CVD started to be used to grow thin films of heterotrimetallic $YBa_2Cu_3O_7$ for which not only there are three metals to deposit, but also arises a difficulty inherent to the CVD of barium.

To make a volatile complex associating two elements having different chemistries, such as a *d* and a *s* or a *f* element, is somewhat challenging. Surprisingly, the first reported volatile heterobimetallic complex was ionic Cs[Y(hfa)$_4$], which Lippard sublimed without decomposition both in air and in vacuum[8]. More recently, Purdy et al. reported the synthesis of heterometallic alkoxides among which NaCu(OCMe$_3$)$_3$ and Na$_2$Cu[OCH(CF$_3$)$_2$]$_4$ start to sublime without decomposition in dynamic vacuum at temperatures as low as 70°C and 90°C respectively, and Ba[Cu(OCMe$_3$)$_3$]$_2$ sublimes at 133−160°C with partial decomposition[9].

A strategy based on the use of alkoxides as bridging ligands and β-diketonates as terminal ligands allowed Hubert-Pfalzgraf et al. to prepare $YBa_3(OtBu)_6(thd)_3$ which sublimes at 190°C/10^{-3} torr[10], BaY$_2$[OCH(CF$_3$)$_2$]$_4$(thd)$_4$, BaCu$_2$[OCH(CF$_3$)$_2$]$_4$(thd)$_2$, and YCu[OCH(CF$_3$)$_2$]$_2$(thd)$_3$ which sublime without decomposition at 150°C/10^{-3} torr, 170°C/10^{-3} torr, 160°C/10^{-3} torr respectively[11]. A $LaNb_3$ complex, [La{OC$_2$H$_4$)$_3$N}$_2${Nb(OPr^i)$_4$}$_3$], which sublimes at about 180−250°C/10^{-1} torr, was obtained using triethanolamine as a bridging ligand and isopropoxide as a terminal ligand[12].

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We present here a thourough study of a new kind of volatile heterobimetallic complexes made from two complexes, Ni(salen) and $Ln(hfa)_3$, which add to form [Ni(salen)-$Ln(hfa)_3$] in which Ni(salen) acts as a bidentate ligand and coordinatively saturates $Ln(hfa)_3$ as confirmed by the crystal structure determination of the gadolinium derivative. This structure determination was part of an investigation of the magnetism of heterobimetallic compounds of general formula [M(salen)$Ln(hfa)_3$] and [M(saloph)$Ln(hfa)_3$], M being Ni or Cu[13]. We observed that [Ni(salen)$Gd(hfa)_3$] could be transported in the vapour phase at 180°C/10^{-2} torr, without decomposition as checked by infra-red and powder X-ray diffraction analyses. We have also established that yttrium and lanthanide derivatives are isostructural. As a preliminary study for qualification as a precursor for MOCVD, we decided to further investigate the thermal behaviour of the yttrium derivative, both in the solid state and in the vapour phase, through thermal analyses (TGA, DTG, DTA), and mass-spectrometry using single-cell and double-cell Knudsen chambers. Thermodynamical parameters relative to sublimation and partial dissociation have been derived. This presentation will be completed with a description of the intermolecular interactions in the solid state, and a brief comparative study with [Cu(saloph)$Gd(hfa)_3$] which proved less easy to sublime despite an alike solid-state structure.

This work is part of an INTAS program on synthesis and application of heterobimetallic complexes as precursors for the preparation of thin film materials by the technique of MOCVD.

Results and Discussion

Crystal and Molecular Structure of [Ni(salen)$Gd(hfa)_3$]

From single crystal studies run for the Gd, Yb and Y derivatives in this work, and the La derivative in a previous work[14], it may be inferred that [Ni(salen)$Y(hfa)_3$] and [Ni-(salen)$Ln(hfa)_3$] for Ln going from La to Yb are isostructural (the Lu derivative was not investigated). They crystallize in the monoclinic system, space group $P2_1/n$, with the following unit-cell constants: a = 17.2(1), b = 22.41(6) A, c = 19.7(3) A, β = 90.4(9)° for La[14]; a = 17.153(1), b = 22.296(2), c = 19.454(2) A, β = 90.36(1)° for Gd; a = 17.29(1), b = 22.349(6), c = 19.59(1) A, β = 90.12(6)° for Y; a = 17.191(3), b = 22.056(6), c = 19.563(4) A, β = 90.18(2)° for Yb. They are isostructural with [Cu(salen)$Gd(hfa)_3$] whose structure has been described in ref.[14] but was not published at the time of this study. Crystal and molecular structures of [Ni(salen)$Gd(hfa)_3$] have been determined as part of an investigation of the magnetic behaviour[13] and of the volatility (this study) of compounds of the [M(salen)$Ln(hfa)_3$] (M = Cu, Ni) series.

The asymmetric unit is made of two symmetrically independent [Ni(salen)$Gd(hfa)_3$] molecules, namely mol__1 and mol__2, paired up into a pseudo-centrosymmetrical dimeric entity in which Ni(salen) moieties overlap, as shown in Figure 1. There are four such dimers per unit-cell. The Ni__1−Ni__2 distance is equal to 3.583(1) A, and the Gd−Ni distances are equal to 3.165(1) A in mol__1 and 3.225(1) A in mol__2. Ni(salen) chelates gadolinium through its oxygen atoms. It is almost planar with atom-to-plane deviations ranging from −0.24 to 0.33 A in mol__1, and −0.40 to 0.24 A in mol__2. The folding angles of the NiO(1)O(2)Gd bridging parts about O(1)O(2) are 52.2(2)° in mol__1 and 47.4(2)° in mol__2. In both molecules, the gadolinium atom is bound to eight oxygen atoms forming a pseudo square antiprism.

A screening of van der Waals contacts gave results shown in Table 1. The shortest contacts between fluorine atoms are larger than 2.8 A, that is more than twice their van der Waals radius of 1.35 A[15]. Examination of H···H distances and C−H···H angles revealed no van der Waals contacts between −CH or $-CH_2$ groups. No π-interactions was no-

Figure 1. Pseudo-centrosymmetrical pairing of molecule__1 and molecule__2 in [Ni(salen)$Gd(hfa)_3$] (letters a, b and c number *hfa* ligands in either molecules)

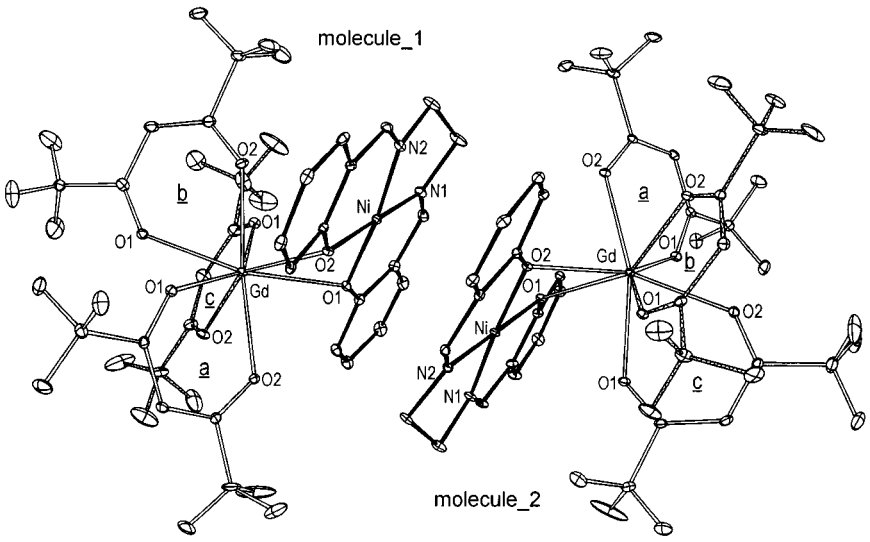


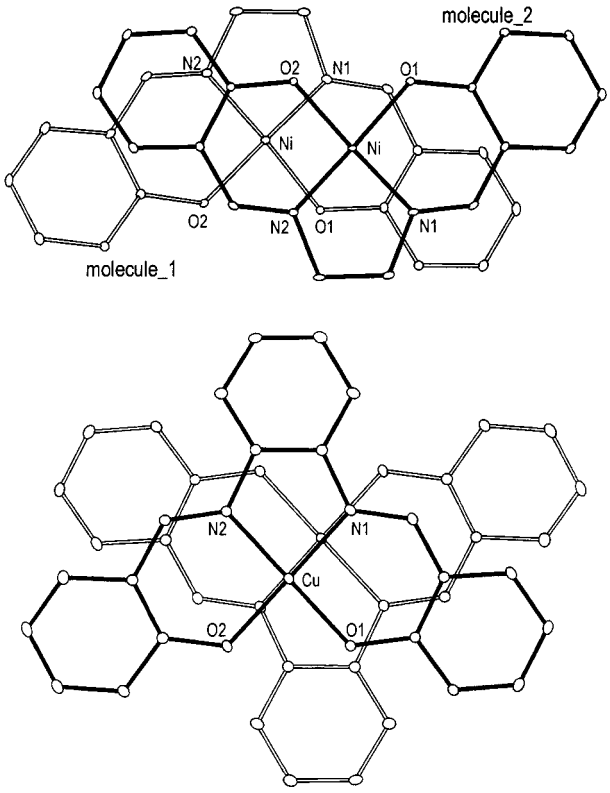
Table 1. Tentative comparison of van der Waals interactions in [Ni(salen)Gd(hfa)$_3$] and [Cu(saloph)Y(hfa)$_3$] (distances in A and angles in deg.). Van der Waals radii are those of Pauling[15]: F, 1.35 A; H, 1.20 A; half-thickness of an aromatic molecule, 1.70 A

	[Ni(salen)Gd(hfa)$_3$]	[Cu(saloph)Y(hfa)$_3$]
Distance between mean planes	3.354(9)	3.291(2) or 3.149(2)[a]
Angle between mean planes	1.1(1)	0
Shortest F···F contacts	none less than 2.82	none less than 2.82
Shortest H···F contacts	none less than 2.61	H19···F31a[i][b]: 2.57(2) H3a···F31c[ii]: 2.55(3)
Shortest −CH···HC− contacts	none less than 2.45	none less than 2.45
−CH···phenyl ring contacts,	H42···C(8−13)1 2.74	none
Contacts between π systems of ajacent M(sal*) entities	none	C(14)···C(18)[i]: 3.55(1) C(17)···C(17)[i]: 3.58(1)

[a] See text. − [b] Code of symmetry operations: [i] $-1-x, -y, -z$; [ii] $-x, -y, 1-z$.

ticed between six-membered rings of ajacent molecules. The main significant interactions occur in the dimers between overlaping Ni(salen) entities. The overlaping scheme of two Ni(salen) entities in a dimer is shown in Figure 2. The mean planes make an angle of 1.1(1)° and are 3.354(8) A apart. This value is slightly less than twice the van der Waals half-thickness of a planar cycle with delocalized π-electrons (1.70 A[15]).

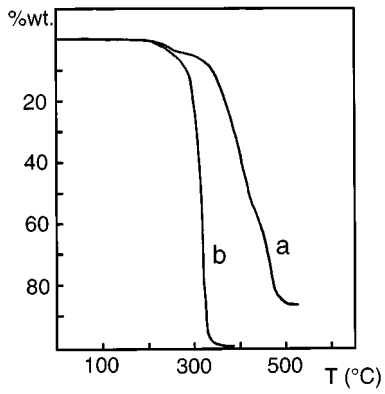
Figure 2. Overlap scheme of two pseudo-centrosymmetrically related Ni(salen) entities in [Ni(salen)Gd(hfa)$_3$] (top), and of two centrosymmetrically related Cu(saloph) entities in [Cu(saloph)Y(hfa)$_3$] (bottom)



Thermal Analyses and Vacuum Sublimation

Thermogravimetric (TGA) curve recorded at 1 atmosphere under nitrogen [Figure 3 (a)] shows that [Ni(salen)Y(hfa)$_3$] is thermally stable up to 210°C, and decomposes in the 210−510°C temperature range. The total loss of weight is about 85% which is consistent with the formation of a 1:1 mixture of YF_3 and NiO. Corresponding DTG-curve showed a six-step process with the main effect occuring at 460°C. Figure 3 (b) shows the thermogravimetric curve recorded under vacuum (0.01 torr). A single-stepped and quasi total (>99%) weight loss occurs in the 220−340°C range. The DTA curve showed a single endothermic peak at about 300°C. This corresponds to sublimation exclusively.

Figure 3. Thermal gravimetric analyses of [Ni(salen)Y(hfa)$_3$] at 1 atm; (a) and under vacuum (b)



Several samples of [Ni(salen)Y(hfa)$_3$] were submitted to isothemal vacuum sublimation (0.01 torr). Freshly prepared product could be totally sublimed at 240°C without decomposition, and an X-ray powder diffraction analysis showed that the sublimate was isostructural with the starting material. A sublimed sample could be sublimed again more than once in the 240−300°C temperature range without decomposition. Air storing over 6 months proved not to affect the sublimation process.

In order to determine whether [Ni(salen)Y(hfa)$_3$] exists in the vapour phase, or if the solid dissociates into gaseous Y(hfa)$_3$ and Ni(salen) which recombine in the cold part of the reactor, mass-spectrometry experiments were carried out, not only for the heterobimetallic complex but also for the component monometallic complexes Y(hfa)$_3$ and Ni(salen).

Table 2. Intensities of main ion currents (relative units) in mass spectra of $Y(hfa)_3$, Ni(salen), and $[Ni(salen)Y(hfa)_3]$ (U = 80 eV)

$Y(hfa)_3$ (341 K)		Ni(salen) (515 K)		$[Ni(salen)Y(hfa)_3]$ (450 K)	
$[Y(hfa) - CF]^+$	0.98	$Ni(salen)^+$	1.00	$[Y(hfa)_3Ni(salen)]^+$	1.00
$Y(hfa)O^+$	0.33	$NiO(C_6H_4)CHNCH_2^+$	0.56	$[Y(hfa)CONi(salen)]^+$	0.75
$[Y(hfa) - 3\ F]^+$	0.17	$NiO(C_6H_4)CH^+$	0.55	$[Y(OH)_2Ni(salen)]^+$	2.4
$[Y(hfa)_2 - 3\ F]^+$	1.00	$Ni(C_6H_4)^+$	0.34	$[Y(hfa)_3 - 3\ F]^+$	1.4
$Y(hfa)_2^+$	0.65	$NiO(C_6H_4)NCH_2^+$	0.29	$Y(hfa)_3^+$	0.18
$[Y(hfa)_3 - 3\ F]^+$	0.30	NiO^+	0.06	$Ni(salen)^+$	19.9
$Y(hfa)_3^+$	0.18			$NiO(C_6H_4)CHNCH_2^+$	2.75
$[Y_2(hfa)_3 - 3\ F]^+$	0.08			$[Y(hfa) - CF]^+$	0.52
$[Y_2(hfa)_5 - 3\ F]^+$	0.13			$NiO(C_6H_4)CH^+$	2.6

Mass Spectrometry Study of $[Ni(salen)Y(hfa)_3]$, $Y(hfa)_3$, and Ni(salen)

The results are displayed in Table 2.

$Y(hfa)_3$: The mass spectrum of $Y(hfa)_3$ shows that the major species are three yttrium-containing ions with m/z of 446 ($[Y(hfa)_2 - 3\ F]^+$), 265 ($[Y(hfa) - CF]^+$), and 503 amu ($[Y(hfa)_2]^+$). Therefore, the saturated vapour over anhydrous $Y(hfa)_3$ mainly consists of monomeric molecules $Y(hfa)_3$. Ions including two yttrium atoms are present as minor species, thus indicating that the vapour phase contains dimeric $[Y(hfa)_3]_2$ molecules too. At 341 K, the respective vapour pressures are $3.9\cdot10^{-3}$ torr ($5.13\cdot10^{-6}$ atm) for $Y(hfa)_3$, and $3.8\cdot10^{-4}$ torr ($5.0\cdot10^{-7}$ atm) for $[Y(hfa)_3]_2$. The enthalpy of dissociation of $[Y(hfa)_3]_2$ in the gas phase according to the equation $[Y(hfa)_3]_{2\,(g)} = 2\ [Y(hfa)_3]_{(g)}$ (*1*) was determined in the 312−365 K temperature range: $\Delta_D H°_T$ = 78.0 kJ/mol. The enthalpy of sublimation of monomeric $Y(hfa)_3$ was also calculated (Table 3).

Table 3. Temperature dependence of saturated vapour pressures of $Y(hfa)_3$, Ni(salen), and $[Ni(salen)Y(hfa)_3]$

Complex	A[a]	B[a]	T range [K]	$\Delta_s H°_T$ [kJ/mol]
$Y(hfa)_3$	4786±500	8.75±0.2	312−365	91.6±8.5
Ni(salen)	7823±350	9.74±0.15	459−545	149.8±7
$[Ni(salen)Y(hfa)_3]$	8894±1000	13.4±0.2	420−471	170.3

[a] A and B are the coefficients of the equation $\log P_{atm} = -A/T + B$.

Ni(salen): Peaks assigned to monomeric species only were detected in the mass spectrum of Ni(salen). At 501 K, the vapour pressure of Ni(salen) is equal to $7.82\cdot10^{-4}$ torr ($1.03\cdot10^{-6}$ atm). The enthalpy of sublimation was calculated (Table 3).

[Ni(salen)Y(hfa)$_3$]: The mass spectrum shows that the vapour phase over $[Ni(salen)Y(hfa)_3]$ contains the heterobimetallic ions $[Y(hfa)_3Ni(salen)]^+$, $[Y(hfa)(CO)Ni(salen)]^+$, $[Y(OH)_2Ni(salen)]^+$, thus indicating that molecules $[Ni(salen)Y(hfa)_3]$ are present in the saturated vapour. However, ion currents corresponding to monometallic species were also detected. A *LAMMA* analysis of the solid residue after sublimation of 50% of the starting material showed the Y/Ni ratio to be still 1:1, from what it may be deduced that $[Ni(salen)Y(hfa)_3]$ sublimes congruously. It may be inferred that monomeric species originate by dissociation of gaseous $[Ni(salen)Y(hfa)_3]$.

$$[Ni(salen)Y(hfa)_3]_{(s)} \rightleftharpoons [Ni(salen)Y(hfa)_3]_{(g)} \quad (2)$$

$$[Ni(salen)Y(hfa)_3]_{(g)} \rightleftharpoons Y(hfa)_{3\,(g)} + Ni(salen)]_{(g)} \quad (3)$$

One notices that the intensities for monometallic Ni species are higher (relative intensity of 19.9 in Table 2) than the ones for bimetallic species. In our opinion, such an unbalanced distribution of relative intensities might result from a dissociative mechanism during the ionization process of $[Ni(salen)Y(hfa)_3]$ (under electron impact) with predominant formation of Ni-containing cationic species. Similar distributions of ion current intensities were observed for volatile $M[Ln(hfa)_4]$ (M = alkaline element)[8] and for complex halogenides of alkaline elements[16].

The temperature dependencies of ion current intensities were studied for heterobimetallic and monometallic species in the mass spectra of $[Ni(salen)Y(hfa)_3]$ in the 420−471 K range. A two-temperature Knudsen chamber was used to study the composition of the unsaturated overheated vapour. It was found that the dissociation process *3* took place in the top part of the chamber. Using these results and assuming a congruent sublimation for $[Ni(salen)Y(hfa)_3]$ − $(P_{[Ni(salen)Y(hfa)3]} + P_{Ni(salen)})/(P_{[Ni(salen)Y(hfa)3]} + P_{Y(hfa)3}) = 1$ and $P_{Ni(salen)} = P_{Y(hfa)3}$ − we calculated the enthalpies for processes *2* and *3*: $\Delta_s H°_T$ = 170.3 ± 21.0 kJ/mole for *2*; $\Delta_D H°_T$ = 127.2 ± 9.0 kJ/mol for *3* (Table 3). A comparison of the latter value with the enthalpy of process *1* shows that $[Ni(salen)Y(hfa)_3]$ is more stable than $[Y(hfa)_3]_2$.

The variation of the equilibrium constant versus temperature for process *3* was determined in the 487−581 K range:

$$\log K_{patm} = -(6643\pm500)/T + (6.33\pm0.3)$$

Table 4 shows partial pressures and vapour phase compositions calculated at 420 and 520 K. In the working tem-

Table 4. Partial pressures [torr] and composition [%] of the vapour phase of $[Ni(salen)Y(hfa)_3]$ at 420 and 520 K

T [K]	$[Ni(salen)Y(hfa)_3]$		Ni(salen)		$Y(hfa)_3$	
420	78%	$1.2\cdot10^{-5}$	11%	$1.7\cdot10^{-6}$	11%	$1.7\cdot10^{-6}$
520	54%	$1.4\cdot10^{-1}$	23%	$6.0\cdot10^{-2}$	23%	$6.0\cdot10^{-2}$

perature range of the present study (420−471 K), the vapour phase over solid [Ni(salen)Y(hfa)$_3$] contains [Ni(salen)-Y(hfa)$_3$] molecules as its main species. However, the partial pressures of the dissociation products, Y(hfa)$_3$ and Ni-(salen), increase rapidly with temperature.

Comparison with [Cu(saloph)Y(hfa)$_3$]: The solid-state structure of [Ni(salen)Ln(hfa)$_3$] shows that part of intermolecular forces to be overcome for vaporization originates with non bonded contacts between Ni(salen) moieties in the pseudo dimers (Figure 1). To discuss this point, it is interesting to make a comparison with [Cu(saloph)Y(hfa)$_3$]. This compound has a structure[13] closely related to the one of [Ni(salen)Gd(hfa)$_3$], but proved less volatile[17]. The *saloph* ligand possesses one more peripheral phenyl ring than *salen*. Like [Ni(salen)Gd(hfa)$_3$], [Cu(saloph)Y(hfa)$_3$] molecules form dimers in which the Cu(saloph) entities overlap. The presence of an extra phenyl ring results in a different overlapping scheme as shown in Figure 2. The molecules are centrosymmetrically related so that the overlapping entities have their mean planes strictly parallel, which is not the case for [Ni(salen)Gd(hfa)$_3$]. The interplanar distance is equal to 3.149(1) A, that is 0.20 A shorter than for the Ni(salen). However, to be more correct it should be noticed that in [Ni(salen)Gd(hfa)$_3$], the phenyl rings are involved in the overlapping scheme, which is not the case for [Cu(saloph)Y(hfa)$_3$]. In this compound, only the three cycles comprising the metal atom overlap while the peripheral phenyl cycles do not. The plane-to-plane distance for the overlapping parts is equal to 3.291(1) A. This is still shorter (by 0.06 A) than for [Ni(salen)Gd(hfa)$_3$]. This shortening most likely results from slightly stronger intermolecular interactions in the *saloph* derivative with respect to the *salen* one. These interactions are all the more efficient that the planes are strictly parallel. They mainly account for the lesser volatility of [Cu(saloph)Y(hfa)$_3$]. Van der Waals contacts between fluorine atoms are very similar in both compounds (Table 1).

Conclusion

[Ni(salen)Ln(hfa)$_3$], which results from the coordination of Ni(salen) to Ln(hfa)$_3$, has proved to sublime congruently. In the working temperature range of this study (420−471 K), the vapour phase contains [Ni(salen)Y(hfa)$_3$] molecules as its main species. At higher temperature, dissociation of gaseous [Ni(salen)Y(hfa)$_3$] into Y(hfa)$_3$ and Ni(salen) increases rapidly with temperature. Therefore, dissociation might play a more or less important role in a MOCVD experiment depending on substrate temperature. It could influence the process of deposition, and it has to be taken into account for a practical use of [Ni(salen)Y(hfa)$_3$] and related complexes in a MOCVD process.

MOCVD experiments are in progress. Since substitution of copper for nickel and/or of one lanthanide for an other one does not change the crystal structure, this kind of complex is expected to be precursors of materials containing both Ni or Cu and Y or a lanthanide element.

Examination of the crystal structure clearly suggests to modify the ligand around Ni in order to prevent dimerization hence increase volatility. This is under current investigation. Complexes of formula [(Ni$_{1-y}$Cu$_y$)(salen)-(Ln$_{1-x}$Ln′$_x$)(hfa)$_3$], which would allow transportation of more than two metal elements in the vapour phase, are being studied too.

Financial support from *INTAS* (contract # 95-118) and the *Russian Fundation for Basic Research* (RFBR) is acknowledged.

Experimental Section

Preparation and Characterization of the Complexes [Ni(salen)Ln(hfa)$_3$], [M = Y (1) and Gd (2)]: Ni(salen) was prepared according to a literature method[18]. For Ln(hfa)$_3$(H$_2$O)$_2$ (Ln = Y, Gd), a procedure adapted from the one described in ref.[19] was used. Elemental analyses (C, H, N) were carried out by the Microanalytical Service of the Universidad Autonoma de Madrid (Spain). IR spectra were taken on a Perkin-Elmer 1750 FTIR spectrophotometer for KBr disks in the 4000−300 cm^{-1} region. Magnetic susceptibility measurements of polycrystalline samples at room temperature were performed with a pendulum-type susceptometer.

Compounds **1** and **2** were synthesized by reaction of Ni(salen) with Ln(hfa)$_3$(H$_2$O)$_2$ in chloroform. A typical preparation is as follows: 0.5 mmol of Ln(hfa)$_3$(H$_2$O)$_2$ dissolved in a minimum amount of chloroform was slowly added under continuous stirring to a hot chloroform solution (50 ml) containing 0.5 mmol of Ni(salen). The orange solution was heated under reflux for 1 hr. Slow evaporation of the resulting solution in a refrigerator yields orange single crystals. − $C_{31}H_{17}F_{18}N_2NiO_8Y$ (**1**) (1035.1): calcd. C 35.93, H 1.65, N 2.70; found C 36.10, H 1.51, N 2.69. − $C_{31}H_{17}F_{18}GdN_2NiO_8$ (**2**) (1103.4): calcd. C 33.59, H 1.54, N 2.53; found C 33.60, H 1.47, N 2.87.

Compound **1** was found diamagnetic whereas a C_MT value (X_M = molar magnetic susceptibility) of 7.90 cm^{3}mol^{-1}K was measured for compound **2** at room temperature. This is consistent with the occurrence of diamagnetic Ni(salen) with a diamagnetic Y^{III} containing unit in **1** and a paramagnetic Gd^{III} containing unit in **2**. IR data for **1** and **2** clearly support the coordination of Ni-(salen) to Ln(hfa)$_3$: shifting towards higher wavenumbers of the C=N stretching vibration and out-of-plane aromatic C−H bend of the *salen* ligand (1622 and 736 cm^{-1} for Ni(salen) to be compared with 1630 and 760 cm^{-1} for **1** and **2**) as well as a splitting of the C=O stretching vibration of the *hfa* ligand (a strong sharp peak at 1647 cm^{-1} for Ln(hfa)$_3$(H$_2$O)$_2$, but two strong sharp peaks at 1663 and 1645 cm^{-1} for **1** and **2**).

X-ray Structure Studies: Gadolinium, ytterbium, and yttrium derivatives of the series [Ni(salen)Ln(hfa)$_3$] were shown to be isomorphous by measuring unit-cell constants from single crystals mounted on an Enraf-Nonius CAD4 diffractometer using Mo-*K*α radiation. The structure of [Ni(salen)Gd(hfa)$_3$] was determined from a single crystal mounted on a Stoe Imaging Plate Diffraction System (IPDS). The structure of [Cu(saloph)Y(hfa)$_3$] was determined from a single crystal mounted on an Enraf-Nonius CAD4 diffractometer. Experimental conditions and structure determinations are reported elsewhere[13].

Thermal Analyses: Samples of [Ni(salen)Y(hfa)$_3$] were submitted to thermal analyses. Thermogravimetric and differential thermogravimetric analyses at the atmospheric pressure were performed in a nitrogen stream, at a heating rate of 5°/min, on a 1500-Q MOM derivatograph. Thermogravimetric and differential thermal analyses under vacuum (0.01 torr) were carried out on a Sinuki-Riko TGD-700 thermal analyzer, at a heating rate of 10°/min. Iso-

thermal dynamic sublimation experiments were run with samples (100 mg) placed in glass test tubes for periods of 30 min. at a pressure of 0.01 torr. Weight losses were determined by gravimetric and complexometric analyses.

Mass Spectrometry and Study of the Vapour Phase: The mass spectra of [Ni(salen)Y(hfa)$_3$], Y(hfa)$_3$, and Ni(salen) were recorded on a MS 1301 spectrometer having a 50−1500 amu mass range, and using 80 eV ionizing electrons. The complexes were vaporized from a Knudsen effusion cell. The ratio of surface of evaporation to surface of the effusion hole was about 600. The cell temperature was measured with a Pt/Pt(Rh) thermocouple (±0.1 K). The experiments were carried out in ranges 312−365 K for Y(hfa)$_3$, 459−545 K for Ni(salen) and 420−471 K for [Ni(salen)Y(hfa)$_3$]. The main molecular ion peaks in mass spectra of Y(hfa)$_3$, Ni(salen), and [Ni(salen)Y(hfa)$_3$] are given in Table 2.

Vapour pressures versus temperature were determined by means of isothermal vaporization experiments and use of the Herz-Knudsen equation. Enthalpies of sublimation were calculated from the temperature dependences of ion current intensities by using Clausius-Clapeyron equation and a least-squares method.

A two-temperature Knudsen cell was used to determine the composition of overheated unsaturated vapour of [Ni(salen)Y(hfa)$_3$]. The saturated vapour was passed from the lower part of a double Knudsen cell to the top part. The temperature of the top part was varied from 487 to 581 K.

Crystallographic data (excluding the structure factor tables) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-101159. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat): +44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] F. Maury, *J. Phys. IV* **1995**, *C5*, 449−463.
[2] F. Maury, *Adv. Mater.* **1991**, *3*, 542−548.
[3] R. A. Fischer, H. D. Kaesz, unpublished observations; R. A. Fischer, H. D. Kaesz, S. I. Khan, H.-J. Müller, *Inorg. Chem.* **1990**, *29*, 1601−1602.
[4] F. Maury, L. Brandt, H. D. Kaesz, *J. Organomet. Chem.* **1993**, *449*, 159−165.
[5] R. A. Fischer, E. Herdtweck, T. Priermeier, *Inorg. Chem.* **1994**, *33*, 934−943, and references therein.
[6] Y. J. Chen, H. D. Kaesz, Y. K. Kim, H.-J. Müller, R. S. Williams, Z. Xue, *Appl. Phys. Lett.* **1989**, *55*, 2760−2761.
[7] B. Fraser, L. Brandt, W. K. Stovall, H. D. Kaesz, S. I. Khan, F. Maury, *J. Organomet. Chem.* **1994**, *472*, 317−328.
[8] S. J. Lippard, *J. Am. Chem. Soc.* **1966**, 88, 4300−4301.
[9] A. P. Purdy, C. F. George, J. F. Callahan, *Inorg. Chem.* **1991**, *30*, 2812−2819.
[10] F. Labrize, L. G. Hubert-Pfalzgraf, J. Vaissermann, C. B. Knobler, *Polyhedron* **1996**, *15*, 577−589.
[11] F. Labrize, L. G. Hubert-Pfalzgraf, J.-C. Daran, S. Halut, P. Tobaly, *Polyhedron* **1996**, *15*, 2707−2718.
[12] V. G. Kessler, LK. G. Hubert-Pfalzgraf, S. Halut, J.-C. Daran, *J. Chem. Soc., Chem. Commun.* **1994**, 705−706.
[13] J. L. Sanz, F. Lloret, M. Julve, A. Gleizes, to be published.
[14] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930−936.
[15] L. Pauling, *Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca (NY), **1960**.
[16] K. A. Kingerich in *Current Topics in Material Science* (Ed.: E. Kaldis), New-York, **1980**, *6*, p. 345.
[17] A. Gleizes, F. Senocq, unpublished observations.
[18] R. H. Bailes, M. Calvin, *J. Am. Chem. Soc.* **1947**, *69*, 1886−1893.
[19] M. F. Richardson, W. F. Wagner, D. E. Dands, *J. Inorg. Nucl. Chem.* **1968**, *30*, 1275−1289.

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