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# Preliminary study of $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$ and $\text{Ni}(\text{en})(\text{hfpd})_2$ as precursors for metalorganic chemical vapour deposition: structural properties and thermal behaviours (en = ethylenediamine, hfpd = hexafluoropentadionato(−))

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## Abstract

$[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  (**1**) and  $\text{Ni}(\text{en})(\text{hfpd})_2$  (**2**) were both obtained by working in the system  $\text{Ni}^{2+}$ /ethylenediamine/hexafluoropentanedione. They have been comparatively studied as possible sources for chemical vapour deposition. Both crystal structures have been determined from single-crystal X-ray diffraction: compound **1** is triclinic, space group  $P\bar{1}$ ,  $a = 9.335(1)$ ,  $b = 12.793(4)$ ,  $c = 8.512(2)$  Å,  $\alpha = 84.28(2)$ ,  $\beta = 109.80(1)$ ,  $\gamma = 104.25(2)^\circ$ , and has an ionic structure; compound **2** is monoclinic, space group  $P2_1/c$ ,  $a = 10.863(8)$ ,  $b = 15.833(6)$ ,  $c = 11.096(9)$  Å,  $\beta = 99.27(4)^\circ$ , and is a neutral complex. Thermal gravimetric analyses have shown that compound **2** could be sublimed under one atmosphere whereas compound **1** could not. Preliminary chemical vapour deposition experiments were carried out under vacuum. Compound **1** gave a coating of  $\text{Ni}_3\text{C}$  in the range 260–310 °C whereas compound **2** gave no coating up to a substrate temperature of 350 °C.

**Keywords:** Crystal structures; Thermal analysis; MOCVD; Nickel complexes

## 1. Introduction

Chemical vapour deposition of materials from metalorganic precursors (MOCVD) requires the use of metal complexes which should meet general conditions such as sublimation without decomposition, easy handling, low or no toxicity, and specific conditions for the material deposited and/or the substrate used. The process of deposition of pure metals or non oxide ceramics such as nitrides and carbides is required to cope with pollution with non metal atoms derived from the organic ligands. Most of the metalorganic sources contain metal–oxygen or metal–carbon bonds.

In this laboratory we have been involved in metallization of organic composite materials by the MOCVD technique. Satisfactorily adherent films of nickel were deposited at nearly 100 °C using nickel tetracarbonyl as a low-temperature decomposing nickel source [1]. The use of nickel tetracarbonyl poses a severe problem of toxicity. Other reported nickel sources are nickelocene [2] and nickel hexafluoropentanedionate [3]. We have started research on volatile

metal complexes possibly containing only metal–nitrogen bonds. Tentative preparations of volatile copper or nickel complexes with  $\text{N}_4$ -donor ligands were carried out starting from ethylenediamine (en) and several  $\beta$ -diketones. Experiments with hexafluoropentanedione (hfpdH) resulted in the preparation of two nickel complexes,  $\text{Ni}(\text{en})(\text{hfpd})_2$  and  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$ , which do not show the expected  $\text{N}_4$  coordination. However, both of them can be sublimed under specific conditions and therefore are potential sources for the deposition of nickel or nickel derivatives.  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  is ionic, whereas  $\text{Ni}(\text{en})(\text{hfpd})_2$  is not. Even if some volatile ionic compounds are known, MOCVD processes reported so far have always used non ionic molecular complexes, as far as we know.

We present here a comparative study of  $\text{Ni}(\text{en})(\text{hfpd})_2$  and  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  in view of their possible use as sources in chemical vapour deposition. This study includes syntheses, crystal structure determinations and thermal gravimetric analyses. Preliminary results of MOCVD experiments will also be reported.

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## 2. Experimental

The 1,1,1,5,5,5-hexafluoropentanedione sample was purchased from Lancaster and used without further treatment. Ethylenediamine was purchased from Aldrich, nickel nitrate hexahydrate, methanol and potassium hydroxide from Pro-labo. IR spectra were recorded as KBr discs on a PerkinElmer spectrometer.

### 2.1. Syntheses

#### 2.1.1. Synthesis of $[Ni(en)_3](CF_3CO_2)_2$ (1)

Two routes are possible:

(a) Ethylenediamine (2.4 g, 40 mmol), nickel nitrate hexahydrate (3.78 g, 13 mmol), hexafluoropentanedione (5.4 g, 26 mmol) and KOH (0.16 g, 2.85 mmol) were successively added in MeOH (15 ml). The reaction mixture was stirred for 2 h under reflux. The solution was then allowed to cool and crystallize. The purple crystalline product was filtered and dried (yield 50%). M.p. 260–265 °C. *Anal. Calc.* for  $NiC_{10}F_6H_{24}O_4N_6$ : C, 25.8; H, 5.16; O, 13.7; N, 18.0. Found: C, 25.5; H, 5.13; O, 13.9; N, 18.1%. IR:  $\nu(C=O)$  1677;  $\nu(NH_2)$  3329;  $\nu(CF)$  1460  $cm^{-1}$ .

(b) Ethylenediamine (2.35 g, 39 mmol) was added to a stirred solution of nickel nitrate hexahydrate (3.78 g, 13 mmol) in MeOH (10 ml). After 1 h, sodium trifluoroacetate (3.54 g, 26 mmol) in MeOH (10 ml) was added. The reaction mixture was stirred for 1 h under gentle heating. After 24 h, purple crystals formed (yield 70%).

#### 2.1.2. Synthesis of $Ni(en)(hfpd)_2$ (2)

Ethylenediamine (40 mmol, 2.4 g) was added to a stirred solution of nickel nitrate hexahydrate (20 mmol, 5.8 g) in MeOH (10 ml). After 30 min, hexafluoropentanedione (8.3 g, 40 mmol) was added. The solution was stirred for 1 h under reflux. A green solid crystallized. Crystals were filtered and dried (yield 57%). M.p. 240 °C. *Anal. Calc.* for  $NiC_{12}F_{12}H_{10}O_4N_2$ : C, 27.0; H, 1.9; O, 12.0; N, 5.25. Found: C, 26.6; H, 2.0; O, 12.5; N, 5.6%. IR:  $\nu(C=O)$  1643;  $\nu(NH_2)$  3338;  $\nu(CF)$  1480  $cm^{-1}$ .

### 2.2. Crystal structure determinations

Crystal systems, accurate cell constants, space groups and intensity data were obtained from single crystals mounted on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo K $\alpha$  radiation.

Crystal data and parameters for data collection and structure refinement are given in Table 1. Intensities were corrected for Lorentz and polarization effects but not for absorption. Structure determinations were carried out by using Patterson and Fourier map techniques, and refined by applying full-matrix least-squares techniques [4]. Throughout the refinement, the minimized function was  $\Sigma(|F_o| - |F_c|)^2$  where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes. Anomalous dispersion

Table 1

Experimental crystal data for  $[Ni(en)_3](CF_3CO_2)_2$  (1) and  $Ni(en)(hfpd)_2$  (2)

	1	2
Formula	$NiC_{10}H_{24}F_6N_6O_4$	$NiC_{12}H_{10}F_{12}N_2O_4$
Molecular weight	465.02	532.89
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Temperature (K)	293	293
<i>a</i> (Å)	9.335(1)	10.863(8)
<i>b</i> (Å)	12.793(4)	15.833(6)
<i>c</i> (Å)	8.512(2)	11.096(9)
$\alpha$ (°)	84.28(2)	
$\beta$ (°)	109.80(1)	99.27(4)
$\gamma$ (°)	104.25(2)	
<i>V</i> (Å <sup>3</sup> )	927(6)	1884(9)
$\rho_{calc}$ (g/cm <sup>3</sup> )	1.67	1.88
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	10.64	10.90
Max. Bragg angle (°)	34	25
Octants collected	<i>h, ±k, ±l</i>	<i>h, k, ±l</i>
Reflections measured	7747	3445
Reflections used	5382	2243
( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))		
Weighting scheme	unit weights	unit weights
Variables	256	286
Max. (shift)/(e.s.d.)	0.09	0.10
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o$	0.048	0.047
$R_w = \{ \Sigma w(F_o - F_c)^2 / \Sigma w F_o^2 \}^{1/2}$	0.054	0.046
$S = [ \Sigma w(F_o - F_c)^2 / (n_o - n_c) ]^{1/2}$	0.88	1.55

effects were included in the calculation of *F* employing the coefficients of Cromer and Waber [5].

All non-H atoms were refined anisotropically. The H atoms were localized and introduced in the refinements as fixed contributors. No significant feature appeared in the final difference Fourier maps. The final reliability factors appear in Table 1. The atomic positional parameters and equivalent isotropic thermal coefficients are listed in Tables 2 and 3.

### 2.3. Analyses

Thermogravimetry analyses were carried out on a SETARAM B85 microbalance controlled by a SETARAM TGC85 programmer. Thermal decomposition was recorded for 80–90 mg samples, under helium with a heating rate of 5 °C/min.  $\theta$ – $\theta$  and grazing incidence X-ray diffraction was performed on a SEIFERT XRD-3000 diffractometer using graphite monochromatized Cu K $\alpha$  radiation.

### 2.4. Chemical vapour deposition

The deposition experiments were carried out in a horizontal, hot-wall, pyrex reactor at reduced pressure ( $3 \times 10^{-2}$  torr) without a carrier gas. A schematic diagram for the experimental setup is shown in Fig. 1. The precursor was loaded at the round end of the reactor. The oven was equipped with a progressive resistance so that a temperature gradient could

Table 2  
Final atomic fractional coordinates and equivalent isotropic displacement parameters for  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  (1)

Atom	x	y	z	B ( $\text{\AA}^2$ )
Ni	-0.15270(5)	0.22148(3)	0.05712(5)	2.26(1)
N(1a)	-0.1308(3)	0.0602(2)	0.1208(3)	2.9(1)
C(1a)	-0.1776(5)	0.0256(3)	0.2701(4)	3.7(2)
C(2a)	-0.1176(5)	0.1196(3)	0.3882(4)	4.0(2)
N(2a)	-0.1812(4)	0.2105(3)	0.2985(3)	3.8(1)
N(1b)	-0.3987(3)	0.1750(3)	-0.0668(3)	3.3(1)
C(1b)	-0.4506(5)	0.2737(4)	-0.1454(6)	4.4(2)
C(2b)	-0.3668(5)	0.3665(3)	-0.0299(6)	4.5(2)
N(2b)	-0.1979(4)	0.3772(2)	0.0112(3)	3.2(1)
N(1c)	-0.1027(4)	0.2125(2)	-0.1689(3)	3.3(1)
C(1c)	0.0664(5)	0.2251(3)	-0.1244(5)	4.0(2)
C(2c)	0.1484(5)	0.3132(3)	0.0039(5)	3.9(2)
N(2c)	0.0918(3)	0.2842(2)	0.1490(3)	3.1(1)
O(1d)	0.4348(4)	0.0698(3)	0.1826(4)	5.9(2)
O(2d)	0.2099(3)	0.0414(3)	0.2335(4)	4.5(1)
C(1d)	0.3486(4)	0.0802(3)	0.2595(4)	3.1(1)
C(2d)	0.4310(5)	0.1534(3)	0.4137(5)	3.7(2)
F(1d)	0.3402(4)	0.1567(4)	0.4997(4)	10.1(2)
F(2d)	0.5605(4)	0.1290(3)	0.5127(4)	6.6(2)
F(3d)	0.4724(5)	0.2541(2)	0.3664(5)	7.5(2)
O(1e)	-0.1571(5)	0.3755(2)	-0.4542(4)	5.8(2)
O(2e)	-0.1164(4)	0.5044(2)	-0.2762(3)	4.5(1)
C(1e)	-0.1649(5)	0.4631(3)	-0.4160(4)	3.4(1)
C(2e)	-0.2479(6)	0.5312(4)	-0.5609(5)	4.3(2)
F(1e)	-0.1995(5)	0.6365(2)	-0.5349(4)	8.5(2)
F(2e)	-0.2279(5)	0.5189(3)	-0.7031(3)	8.2(2)
F(3e)	-0.3961(4)	0.5081(5)	-0.5897(6)	11.7(3)

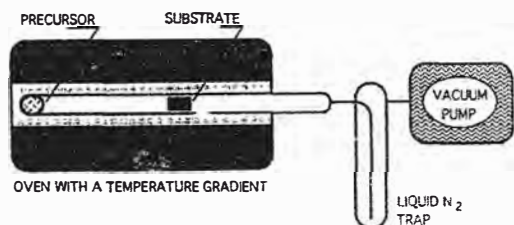


Fig. 1. Diagram of the experimental setup for the MOCVD experiment.

be set up from the temperature of sublimation of the source to a maximum approximatively at the middle of the oven. The temperature of any position in the reactor was read from preliminary calibration. Reaction by-products were trapped downstream in a liquid nitrogen cooled trap. Experiments were carried out for a period of 5 h, and films were formed both on silicon and/or glass substrates placed into the reactor, and on the walls of the pyrex reactor itself in the hot zone of the oven.

### 3. Results and discussion

#### 3.1. Syntheses

Under the conditions described in Section 2, it was not possible to produce either ketoimine nor  $\beta$ -diimine deriva-

Table 3  
Final atomic fractional coordinates and equivalent isotropic displacement parameters for  $\text{Ni}(\text{en})(\text{hfpd})_2$  (2)

Atom	x	y	z	B ( $\text{\AA}^2$ )
Ni	0.24194(6)	0.01996(5)	-0.01860(6)	3.63(1)
O(1a)	0.3220(3)	-0.0268(3)	-0.1597(3)	4.6(2)
O(2a)	0.1076(3)	0.0783(3)	-0.1449(3)	4.2(2)
O(1b)	0.1665(3)	0.0685(3)	0.1242(3)	4.3(2)
O(2b)	0.3534(3)	0.1258(3)	-0.0127(3)	4.6(2)
F(1a)	0.3390(5)	-0.0365(4)	-0.4656(3)	10.6(3)
F(2a)	0.4757(4)	-0.0609(4)	-0.3157(4)	11.6(4)
F(3a)	0.3253(6)	-0.1393(4)	-0.3609(6)	13.4(5)
C(1a)	0.3591(6)	-0.0611(5)	-0.3536(6)	5.6(4)
C(2a)	0.2836(5)	-0.0130(4)	-0.2694(5)	3.8(2)
C(3a)	0.1870(5)	0.0362(4)	-0.3227(5)	4.3(3)
C(4a)	0.1055(5)	0.0773(3)	-0.2565(5)	3.7(3)
C(5a)	-0.0006(5)	0.1253(5)	-0.3328(6)	5.0(3)
F(4a)	0.0368(4)	0.1806(3)	-0.4038(5)	10.4(3)
F(5a)	-0.0649(4)	0.1706(4)	-0.2676(5)	10.9(3)
F(6a)	-0.0772(5)	0.0788(3)	-0.3972(7)	13.9(4)
F(1b)	0.1894(5)	0.0886(3)	0.3789(3)	8.9(3)
F(2b)	0.0207(4)	0.343(3)	0.2739(4)	8.2(3)
F(3b)	0.1632(4)	0.2198(3)	0.3491(3)	6.6(2)
C(1b)	0.1419(6)	0.1451(4)	0.2972(5)	4.8(3)
C(2b)	0.2024(5)	0.1336(4)	0.1817(4)	3.5(2)
C(3b)	0.2872(5)	0.1936(4)	0.1583(5)	4.0(3)
C(4b)	0.3549(5)	0.1841(4)	0.0613(5)	3.8(3)
C(5b)	0.4476(6)	0.2550(5)	0.0480(7)	5.2(3)
F(4b)	0.5580(4)	0.2360(3)	0.1056(5)	8.5(3)
F(5b)	0.4616(5)	0.2649(4)	-0.0652(4)	11.2(4)
F(6b)	0.4196(5)	0.3270(3)	0.0881(7)	12.5(4)
N(1)	0.1318(4)	-0.0861(3)	-0.0084(4)	4.3(2)
C(1)	0.2139(6)	-0.1562(4)	0.0408(6)	5.5(3)
C(2)	0.3119(6)	-0.1222(5)	0.1424(6)	5.8(4)
N(2)	0.3752(4)	-0.0497(3)	0.0957(4)	4.8(2)

tives. It has long been known that in addition to undergoing Schiff base condensation with amines, square planar  $\beta$ -diketonates of transition metals form adducts with monodentate and chelating ligands [6]. This is well illustrated by the formation of  $\text{Ni}(\text{en})(\text{hfpd})_2$  in the present study.

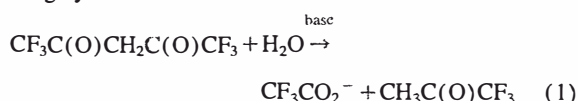
The preparation of  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  by reacting  $\text{Ni}^{2+}$ , en, and hfpdH in the presence of  $\text{OH}^-$  illustrates another alternative to Schiff base condensation. Even if scarcely documented, generation of trifluoroacetate from hexafluoroacetylacetonate might have been expected since it was first reported in 1979 by Fackler and co-workers [7] who observed the formation of  $\text{Cu}(\text{CF}_3\text{CO}_2)_2(\text{py})_4$  and  $\text{Cu}(\text{CF}_3\text{CO}_2)_2(\text{py})_2$  from a pyridine solution of  $\text{Cu}(\text{hfpd})_2$  in contact with the atmosphere for several weeks. Recently, Williams and co-workers [8] observed the unexpected formation of  $\{[\text{Tb}_2(\text{hfpd})_4(\mu_2\text{-O}_2\text{CCF}_3)_2(\text{H}_2\text{O})_4][\text{Tb}(\text{hfpd})_3(\text{H}_2\text{O})_2]_2 \cdot \text{H}_2\text{O}\}$  by reacting NaOH, hfpdH and  $\text{TbCl}_3(\text{H}_2\text{O})_6$  in methanol. Hubert-Pfalzgraf and co-workers [9] observed the same kind of transformation concerning non fluorinated acetylacetonato species. By reacting  $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$  and acetylacetonate in toluene, these authors have obtained  $\text{Y}_2(\text{OAc})_2(\text{acac})_4(\text{H}_2\text{O})_2$ . They have suggested that "generation of the acetato moieties is probably due to

Table 4  
Selected interatomic distances (Å) and bond angles (°) for [Ni(en)<sub>3</sub>][CF<sub>3</sub>COO]<sub>2</sub> (**1**)

Around Ni					
	i = a	i = b	i = c		
Ni–N(1i)	2.122(3)	2.133(3)	2.148(3)		
Ni–N(2i)	2.146(3)	2.108(3)	2.117(3)		
Ethylenediamine ligands					
	i = a	i = b	i = c		
N(1i)–C(1i)	1.473(5)	1.479(5)	1.464(5)		
C(1i)–C(2i)	1.516(5)	1.498(6)	1.517(5)		
C(2i)–N(2i)	1.465(5)	1.469(5)	1.481(5)		
Ni–N(1i)–C(1i)	109.1(2)	107.0(2)	107.6(2)		
N(1i)–C(1i)–C(2i)	108.4(3)	109.6(3)	108.8(3)		
C(1i)–C(2i)–N(2i)	108.0(2)	108.3(4)	108.6(3)		
C(2i)–N(2i)–Ni	107.1(3)	108.1(2)	108.0(2)		
CF <sub>3</sub> COO <sup>−</sup> anions					
	i = d	i = e			
C(1i)–O(1i)	1.233(6)	1.242(4)			
C(1i)–O(2i)	1.218(4)	1.223(5)			
C(1i)–C(2i)	1.549(5)	1.534(5)			
C(2i)–F(1i)	1.304(6)	1.326(5)			
C(2i)–F(2i)	1.308(5)	1.315(6)			
C(2i)–F(3i)	1.315(5)	1.283(6)			
O(1i)–C(1i)–O(2i)	130.1(3)	129.2(3)			
O(1i)–C(1i)–C(2i)	114.4(3)	115.4(3)			
O(2i)–C(1i)–C(2i)	115.5(4)	115.4(3)			
C(1i)–C(2i)–F(1i)	113.2(3)	113.5(3)			
C(1i)–C(2i)–F(2i)	113.5(4)	113.8(4)			
C(1i)–C(2i)–F(3i)	110.3(3)	111.7(4)			
F(1i)–C(2i)–F(2i)	109.7(3)	104.5(3)			
F(1i)–C(2i)–F(3i)	104.2(4)	106.6(5)			
F(2i)–C(2i)–F(3i)	105.2(3)	106.1(4)			
H bonding					
N(1a)...O(2d)	3.059(4)	N(1b)...O(1d) <sup>iii</sup>	3.061(5)	N(1c)...O(2e) <sup>iv</sup>	3.031(4)
N(1a)...O(2d) <sup>i</sup>	3.184(4)	N(2b)...O(1e) <sup>iv</sup>	3.012(4)	N(1c)...O(2d) <sup>i</sup>	3.199(4)
N(2a)...O(2e) <sup>ii</sup>	3.045(5)	N(2b)...O(1e)	3.162(3)	N(2c)...O(1e)	2.941(4)

Code of equivalent positions: <sup>i</sup>:  $-x, -y, -z$ ; <sup>ii</sup>:  $-x, 1-y, 1-z$ ; <sup>iii</sup>:  $x-1, y, z$ ; <sup>iv</sup>:  $-x, 1-y, -z$ .

retro-Claisen type reactions (Eq. (1)) [10] induced either by trace amounts of alkoxo or hydroxo anions stabilized by a highly basic medium<sup>††</sup>.



The production of trifluoroketone was indirectly proved by Wang et al. in their synthesis of the 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato ligand [11]. The reactions might involve the intermediate formation of a derivative of the CF<sub>3</sub>C(O)CHC(O)(OH)CF<sub>3</sub><sup>−</sup> anion as suggested by the works of Fukuda et al. [12] and of van Eldik and co-workers [13] on the addition of OH<sup>−</sup> to the hexafluoropentanedionato ligand coordinated to Co(III).

The direct synthesis of [Ni(en)<sub>3</sub>]<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> using a trifluoroacetate salt is described in Section 2.

### 3.2. Description and comparison of the structures

Selected bond lengths and angles for **1** are given in Table 4. The crystal structure is centrosymmetrical. It consists of

two cations [Ni(en)<sub>3</sub>]<sup>2+</sup> and two symmetrically independent pairs of trifluoroacetate anions per unit cell. A view of the cation with its next neighboring anions (see below) is given in Fig. 2 with the labeling scheme. All the atoms occupy general positions. Cation isomer pairs have conformations Δλλλ and Λδδδ as in other known solid state derivatives of the [Ni(en)<sub>3</sub>]<sup>2+</sup> cation [14]. Bond lengths and angles show no unusual values. The Ni–N bond lengths are in the range 2.13 ± 0.02 Å around the mean value. The N–C–N dihedral angles measure 57.3(5), 56.4(4) and 56.6(4)° for rings a, b and c respectively, the average value being 56.8(4)°. A screening of intermolecular contacts (Table 4) evidences hydrogen bonds between anion oxygens and cation nitrogens, so that a cation is surrounded by six anions (Fig. 2).

Selected bond lengths and angles for **2** are given in Table 5. The structure consists of four neutral molecules Ni(en)(hfpd)<sub>2</sub> per unit cell. A view of the molecule is shown in Fig. 3 with the labeling scheme. The Ni–O bond lengths range from 2.047(4) to 2.070(3) Å, and the two Ni–N bonds

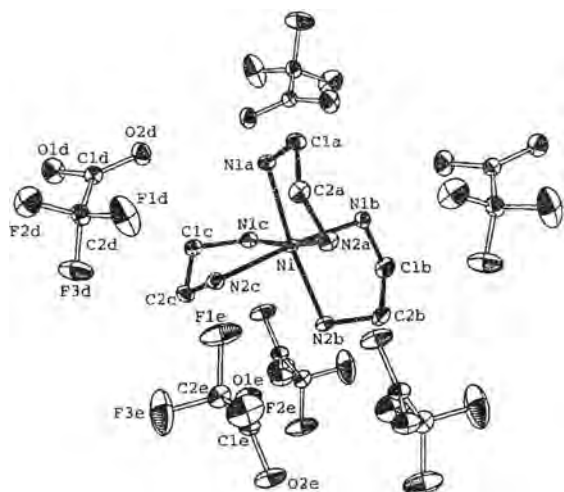


Fig. 2. ORTEP view of the  $\text{Ni}(\text{en})_3^{2+}$  cation with its six next nearest neighboring  $\text{CF}_3\text{CO}_2^-$  anions in  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  (**1**) (20% probability thermal ellipsoids).

(2.076(5) and 2.081(5) Å) are 0.05 Å shorter on the average than in **1**. The N–C–N dihedral angle measures  $53.6(4)^\circ$  that is about  $3^\circ$  less than the average value measured for **1**. Intermolecular contacts (Table 5) are weaker than in **1**: they consist of van der Waals interactions between fluorine atoms with no contact closer than 2.93 Å, and hydrogen bonds with no hydrogen–fluorine or hydrogen–oxygen distance smaller than 2.26 Å. It is also worthwhile to note the presence of intramolecular H bonding between the  $-\text{NH}_2$  groups and two of the ketonato oxygens (Table 5). The geometry of the complex compares with those of (1,2-diaminoethane)-bis(1,3-diphenyl-1,3-propanedionato)nickel(II) [15] and of [*N,N'*-diphenyl-1,2-diaminoethane]bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel(II) [16].

### 3.3. Thermal gravimetric analyses

Thermogravimetric analyses were performed under one atmosphere of helium. Both compounds undergo one major stage of weight loss upon heating. For  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$ , the major weight loss occurs at 180–285 °C (Fig. 4). A second, very smooth one follows, corresponding to about 6% of the total weight loss. Constant weight was observed only after standing at about 600 °C for 30 min. The final residue was a black powder which proved to contain nickel from X-ray diffraction. The residual weight (15.1%) is significantly higher than the expected amount of nickel (12.6% from the formula  $\text{NiC}_{10}\text{H}_{24}\text{F}_6\text{N}_6\text{O}_4$ ), which implies the possible presence of amorphous carbon. It also shows that decomposition is mainly responsible for the weight loss upon heating compound **1** under one atmosphere.

$\text{Ni}(\text{en})(\text{hfpd})_2$  undergoes a major stage of weight loss at 100–285 °C (Fig. 5). Constant weight was achieved at 575 °C after one more, very smooth loss of weight representing about 1% of the total weight loss. As for compound **1**, the

final residue was a black powder containing nickel from X-ray diffraction. It is worth pointing out that the residual weight represented only 0.6% of the initial weight implying

Table 5  
Selected interatomic distances (Å) and bond angles ( $^\circ$ ) for  $\text{Ni}(\text{hfpd})_2(\text{en})$  (**2**)

Around Ni					
Ni–N(1)	2.076(5)	Ni–O(1a)	2.048(4)	Ni–O(1b)	2.048(4)
Ni–N(2)	2.081(5)	Ni–O(2a)	2.070(3)	Ni–O(2b)	2.062(4)
Hexafluoropentanedionato ligands					
		i = a		i = b	
C(1i)–F(1i)		1.288(8)		1.317(7)	
C(1i)–F(2i)		1.270(8)		1.312(8)	
C(1i)–F(3i)		1.290(10)		1.320(7)	
C(1i)–C(2i)		1.540(9)		1.542(8)	
C(2i)–O(1i)		1.241(6)		1.241(7)	
C(2i)–C(3i)		1.363(7)		1.376(8)	
C(3i)–C(4i)		1.398(8)		1.405(8)	
C(4i)–O(2i)		1.235(6)		1.235(7)	
C(4i)–C(5i)		1.520(8)		1.531(9)	
C(5i)–F(4i)		1.287(9)		1.301(7)	
C(5i)–F(5i)		1.299(9)		1.299(9)	
C(5i)–F(6i)		1.247(8)		1.278(9)	
F(1i)–C(1i)–F(2i)		108.9(6)		108.5(6)	
F(1i)–C(1i)–F(3i)		103.2(6)		106.6(5)	
F(2i)–C(1i)–F(3i)		106.4(7)		107.6(5)	
F(1i)–C(1i)–C(2i)		114.3(6)		108.6(5)	
F(2i)–C(1i)–C(2i)		113.5(5)		111.7(5)	
F(3i)–C(1i)–C(2i)		109.9(6)		113.6(5)	
C(1i)–C(2i)–C(3i)		117.9(5)		117.6(5)	
C(1i)–C(2i)–O(1i)		112.3(5)		112.6(5)	
O(1i)–C(2i)–C(3i)		129.8(5)		129.8(5)	
C(2i)–C(3i)–C(4i)		123.1(5)		121.3(5)	
O(2i)–C(4i)–C(3i)		128.4(5)		129.6(5)	
C(5i)–C(4i)–O(2i)		116.3(5)		115.0(5)	
C(5i)–C(4i)–C(3i)		115.3(5)		115.4(5)	
F(4i)–C(5i)–C(4i)		113.3(5)		110.6(6)	
F(5i)–C(5i)–C(4i)		113.2(5)		111.3(6)	
F(6i)–C(5i)–C(4i)		113.5(6)		115.0(6)	
F(4i)–C(5i)–F(5i)		102.5(6)		105.2(6)	
F(4i)–C(5i)–F(6i)		107.4(6)		106.8(6)	
F(5i)–C(5i)–F(6i)		106.1(6)		107.5(7)	
Ni–O(1i)–C(2i)		124.7(4)		125.3(4)	
Ni–O(2i)–C(4i)		124.8(3)		125.0(4)	
Ethylenediamine ligands					
N(1)–C(1)	1.472(8)	Ni–N(1)–C(1)		108.0(3)	
C(1)–C(2)	1.518(9)	N(1)–C(1)–C(2)		108.6(5)	
C(2)–N(2)	1.474(9)	C(1)–C(2)–N(2)		109.0(5)	
		C(2)–N(2)–Ni		108.0(3)	
Intramolecular H bonds					
N(1)...O(1b)		2.851(6)			
N(2)...O(1a)		2.823(6)			
Intermolecular H bonds					
C(3a)...F(1b) <sup>i</sup>		3.418(7)			
N(1)...F(2b) <sup>ii</sup>		3.229(6)			
N(1)...O(2a) <sup>iii</sup>		3.331(6)			
C(1)...F(4b) <sup>iv</sup>		3.416(8)			
N(2)...F(2a) <sup>iv</sup>		3.221(7)			
N(2)...O(2b) <sup>iv</sup>		3.444(7)			

Code of equivalent positions: <sup>i</sup>:  $x, y, z-1$ ; <sup>ii</sup>:  $1-x, -1/2+y, -1/2-z$ ; <sup>iii</sup>:  $-x, -y, -z$ ; <sup>iv</sup>:  $1-x, -y, -z$ .

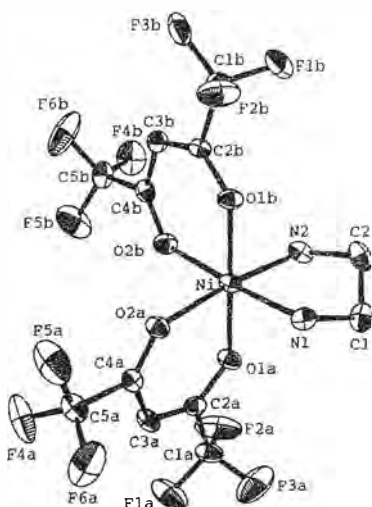


Fig. 3. ORTEP view of the molecular structure of  $\text{Ni}(\text{en})(\text{hfpd})_2$  (**2**) (20% probability thermal ellipsoids).

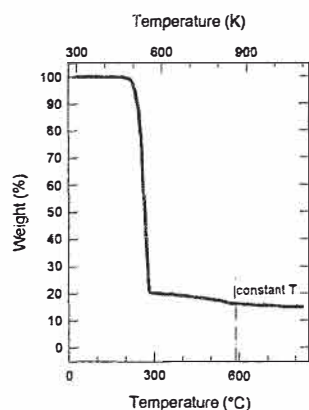


Fig. 4. Thermal gravimetric analysis diagram for  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  (**1**).

that sublimation is mainly responsible for the weight loss upon heating compound **2** under one atmosphere.

### 3.4. Deposition experiments and discussion

Preliminary deposition experiments were conducted at reduced pressure (0.03 torr) with dynamic pumping and without a gas carrier, using the setup described in Section 2 (Fig. 1) since none of the conventional reactors in use in this laboratory was available at the time of these experiments. The precursors were heated to 110 °C for  $\text{Ni}(\text{en})(\text{hfpd})_2$  and 140 °C for  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  and the highest substrate temperature used was 350 °C.

With  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  deposition occurred over the range 260–310 °C, yielding a dark grey, metallic luster coating on the wall of the reactor. X-ray diffraction was performed on chips of coating collected from the reactor wall, and on thin films grown on silicon or glass substrates. Chips were powdered and analyzed using  $\theta$ - $\theta$  recording of the diffraction

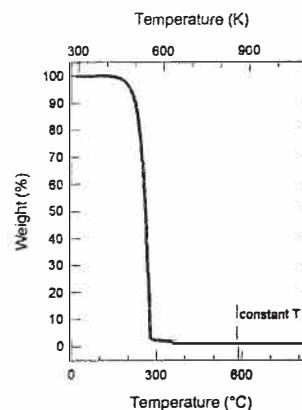


Fig. 5. Thermal gravimetric analysis diagram for  $\text{Ni}(\text{en})(\text{hfpd})_2$  (**2**).

lines, whereas grazing incidence was used for the thin films. All the samples proved to contain nickel carbide  $\text{Ni}_3\text{C}$  as their only crystalline phase. For  $\text{Ni}(\text{en})(\text{hfpd})_2$ , no significant deposit was observed in the range of temperature used.

The results of TGA and preliminary CVD experiments evidence two facts. First,  $[\text{Ni}(\text{en})_3]\text{CF}_3\text{CO}_2$  shows nearly no volatility under one atmosphere, but at 0.03 torr and 140 °C it yields a vapour phase which can be used for CVD. What the chemical composition is of this phase with regard to that of the solid state ionic compound is an open question. The second fact is that  $\text{Ni}(\text{en})(\text{hfpd})_2$  can be sublimed with a very low decomposition rate under one atmosphere, but gives a gas phase which is thermally more stable than that given by compound **1** since no significant deposition was observed at about 350 °C under vacuum. In  $\text{Ni}(\text{en})(\text{hfpd})_2$ , the presence of amino  $-\text{NH}_2$  groups bound to nickel gives rise to intramolecular H bonds towards ketonato oxygen atoms as reported in the description of the structure. This might account for strengthening of the thermal stability. It was also noticed that the Ni–N bonds are significantly shorter by about 0.05 Å in  $\text{Ni}(\text{en})(\text{hfpd})_2$  (two bonds measuring 2.08 Å), hence stronger, than in  $[\text{Ni}(\text{en})_3](\text{CF}_3\text{CO}_2)_2$  (six bonds in the range 2.11–2.15 Å). Whether this is related to the presence of the intramolecular H bonds or results from heterolepticity is difficult to decide. This is all the more difficult as there are no available data about Ni–O bond lengths in  $\text{Ni}(\text{hfpd})_2$  to make a comparison.

## 4. Conclusions

Tris(ethylenediamine)nickel(II) trifluoroacetate, a non sublimable ionic compound under one atmosphere, gives a nickel carrier gas phase under reduced pressure, and can be used as a precursor in the MOCVD technique. Thin films of  $\text{Ni}_3\text{C}$  have been deposited from it at 260–310 °C on silicon and glass substrates. (Ethylenediamine)bis(hexafluoropentanedionate)nickel(II), a neutral complex which can be sublimed under one atmosphere, shows higher thermal stability, yielding no deposit at temperatures around 350 °C.



Both these compounds were obtained by working in the system Ni(II)/hexafluoropentanedione/ethylenediamine. The ionic derivative resulted from a retro-Claisen reaction. Nickel and nickel carbide (Ni<sub>3</sub>C) MOCVD experiments using conventional reactors with a carrier gas are currently carried out and will be reported elsewhere [17].

## 5. Supplementary material

Tables S1–S6 listing H-atom positions, anisotropic thermal coefficients, complete lists of bond lengths and angles (8 pages) and Tables S7–S8 listing calculated and observed structure factors (10 pages) are available from the authors on request

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