

Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary

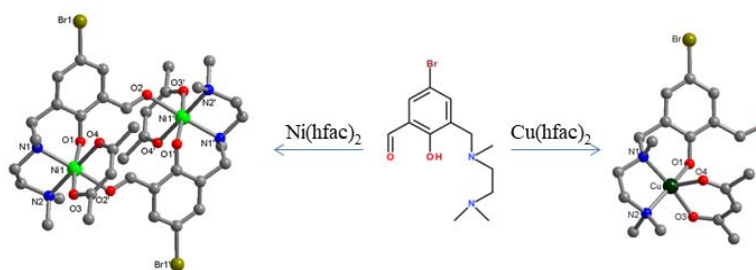
NEW MIXED LIGAND COMPLEXES RESULTING FROM THE REACTION OF β -DIKETONATO DERIVATIVES WITH A MANNICH BASE

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Three new compounds have been synthesized and characterized: $[\text{Co}_2(\text{L})_2(\text{hfac})_2]$ (**1**), $[\text{Ni}_2(\text{L})_2(\text{hfac})_2]$ (**2**), and $[\text{Cu}(\text{L})(\text{hfac})]$ (**3**) [HL is the Mannich base resulting from reaction of 5-bromosalicylaldehyde with formaldehyde and N,N,N'-trimethylethylenediamine and hfac⁻ is the hexafluoroacetylacetonato ligand]. All compounds have been obtained by reacting the Mannich base with $\text{M}(\text{hfac})_2$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+}). Complexes **1** and **2** are isostructural homodinuclear compounds, while complex **3** is a mononuclear compound. Complex **2** results from two $\{\text{Ni}(\text{L})(\text{hfac})\}$ units connected by carbonyl groups.



INTRODUCTION

Hexafluoroacetylacetonato complexes are useful starting materials for designing homo- and heterometallic polynuclear systems.¹ These reactions occur either with the preservation of all hfac⁻ groups or by replacing one of them with another anionic ligand.^{1a,b,2} The hexafluoroacetylacetonato ligand increases the Lewis acidity of the $\text{M}^{\text{n}+}$ ions, and facilitates the coordination of other molecules, even if their coordination ability is weak.³ For example, nitronyl-nitroxides⁴ or tempo⁵ derivatives can be easily coordinated to the metal centers from $\text{M}(\text{hfac})_n$ complexes. The coordination of nitriles is also facilitated, as we have shown in a recent paper.³

The Mannich reaction is an excellent source of ligands. It starts from an aldehyde, paraformaldehyde

and a secondary amine, resulting in multidentate ligands.⁶ The number of donor atoms is pre-established by choosing the appropriate starting materials.

In a recent paper we have shown how hexafluoroacetylacetonato complexes used as starting materials lead to complexes with various nuclearities. For example, by reacting $[\text{M}(\text{hfac})_2(\text{H}_2\text{O})_n]$ with preformed Schiff-base complexes, three compounds have been obtained: $[\text{Cu}_2(\text{saldmpn})_2(\mu\text{-OCH}_3)_2\text{Cu}_2(\text{hfac})_2]$, $[\text{Ni}_2(\text{valaepy})_2(\text{hfac})_2]$, and $[\text{Cu}(\text{saldmpn})\text{Co}(\text{hfac})_2]$.⁷

Herein, we report the synthesis and characterization of three new coordination compounds, which are obtained starting from a Mannich base and $\text{M}(\text{hfac})_n$ complexes.

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EXPERIMENTAL

Materials and methods

All reagents and solvents for synthesis were commercially purchased and used without any further purification. Elemental analyses of C, N and H were performed on a EuroEa Elemental Analyzer. IR spectra were recorded on a FTIR Bruker Tensor V-37 spectrophotometer (KBr pellets) in the range of 4000–400 cm^{-1} . UV–Vis diffuse reflectance spectra were recorded on a JASCO V-670 spectrophotometer.

Synthesis of the Mannich base (HL)

The synthesis of the organic pro-ligand (HL) starts from 5-bromosalicylaldehyde, which reacts with formaldehyde and N,N,N' -trimethylethylenediamine according to the procedure previously described.⁸

Synthesis of $[\text{Co}_2(\text{L})_2(\text{hfac})_2]$ (1)

To a methanolic solution (20 mL) of HL (0.0312 g, 0.1 mmol), a solution of $\text{Co}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ in 5 mL methanol (0.0473 g, 0.1 mmol) was added under stirring resulting an orange mixture. The resulting solution was stirred for about 1 h and then filtered. After 2 week, red crystals suitable for X-ray diffraction have been obtained. Elemental analysis: Calcd. for $\text{C}_{36}\text{H}_{42}\text{N}_4\text{O}_8\text{F}_{12}\text{BrCo}_2$: C, 39.85; H, 3.87; N, 5.6%. Found: C, 38.75, H, 3.56, N, 5.12%. Selected IR peaks (KBr disk/ cm^{-1}): 1650(s), 1614(s), 1547(m), 1468(s), 1391(m), 1253(vs), 1223(s), 1201(s), 1145(vs).

Synthesis of $[\text{Ni}_2(\text{L})_2(\text{hfac})_2]$ (2)

Compound **2** is isostructural with compound **1** and was synthesized in a similar way dissolving the HL ligand (0.0312 g, 0.1 mmol) in 20 mL acetonitrile. After the deprotonation of HL with triethylamine, a solution of

$\text{Ni}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ (0.0473 g, 0.1 mmol) in acetonitrile (5 mL) was added under continuous stirring. The green solution was stirred for about 1 h, filtered and let to crystallize at room temperature. After a couple of weeks, green crystals are formed. Elemental analysis: Calcd. for $\text{C}_{36}\text{H}_{42}\text{N}_4\text{O}_8\text{F}_{12}\text{BrNi}_2$: C, 39.85; H, 3.87; N, 5.6%. Found: C, 39.52, H, 3.63, N, 5.23%. Selected IR peaks (KBr disk/ cm^{-1}): 1652(s), 1610(vs), 1546(m), 1502(m), 1472(s), 1410(m), 1253(vs), 1224(s), 1201(s), 1105(vs).

Synthesis of $[\text{Cu}(\text{L})(\text{hfac})]$ (3)

The Mannich base (0.0312 g, 0.1 mmol) was dissolved in 20 mL methanol and deprotonated with triethylamine. To the yellow solution of the ligand, a $\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$ (0.0477 g, 0.1 mmol) solution in methanol was added under continuous stirring. The molar ratio between HL and Cu^{2+} is 1:1. The final green solution was stirred for about 1 h, filtered and let to crystallize at room temperature. After 2 weeks, dark green crystals suitable for X-ray diffraction have been obtained. Elemental analysis: Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_4\text{F}_6\text{BrCu}$: C, 36.79; H, 3.57; N, 4.77%. Found: C, 34.94; H, 3.65; N, 4.52%. Selected IR peaks (KBr disk/ cm^{-1}): 1676(s), 1655(s), 1544(m), 1519(m), 1503(m), 1458(s), 1253(vs), 1201(s), 1148(vs).

X-Ray crystallography

Suitable single crystals for crystallographic data collection were obtained by slow evaporation of the solvent, as described above. X-ray studies were performed on a STOE IPDS II diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and they were refined with the ShelXL refinement package.⁹ Data collection and refinement parameters for the three compounds are summarized in Table 1. CCDC reference numbers: 1851451 (**2**) and 1851452 (**3**).

Table 1

Crystallographic data for compounds **2** and **3**

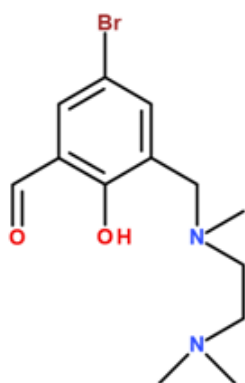
Compound	2	3
Formula	$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_8\text{F}_{12}\text{Br}_2\text{Ni}_2$	$\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4\text{F}_6\text{BrCu}$
Formula weight/ g mol^{-1}	1159.94	584.80
T/K	293	293
$\lambda/\text{\AA}$	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
$a/\text{\AA}$	9.116(2)	9.656(2)
$b/\text{\AA}$	11.21(2)	10.542(3)
$c/\text{\AA}$	11.851(3)	11.990(3)
α/deg	80.975(18)	82.57(2)
β/deg	68.550(17)	68.70(2)
γ/deg	85.167(18)	86.25(2)
$V/\text{\AA}^3$	1113(2)	1127.4(5)
Z	1	2
Calculated density/ g cm^{-3}	1.731	1.723
Absorption coefficient/ cm^{-1}	2.743	2.817
$F(000)$	580	582
Crystal size/ $\text{mm} \times \text{mm} \times \text{mm}$	0.5 x 0.3 x 0.15	0.2 x 0.1 x 0.1
θ range/deg	2.402 to 25.999	2.348 to 24.999
Limiting indices	-9<h<11, -13<k<13, -14<l<14	-11<h<11, -12<k<11, -14<l<14
Collected reflections	8541	12516

Table 1 (continued)

Symmetry independent reflections	4209	3919
R_{int}	0.0860	0.1659
Completeness/%	96.9	95.7
Max and min transmission	0.7073 and 0.4260	1.2734 and 0.8815
Data/restraints/ parameters	4209 / 0 / 289	3919 / 3 / 289
GOF on F^2	1.101	0.659
Final R indices	$R1 = 0.0991$ $wR2 = 0.1967$	$R1 = 0.0771$ $wR2 = 0.1642$
Largest diff peak and hole/ $e \text{ \AA}^{-3}$	0.977 and -1.588	0.873 and -0.365

RESULTS AND DISCUSSION

The three new complexes have been obtained following the same general procedure. In all cases one of the hfac⁻ ligands has been replaced by the anionic Mannich-base ligand. From the reactions between β -diketonato complexes, [Co(hfac)₂(H₂O)₂], [Ni(hfac)₂(H₂O)₂], and [Cu(hfac)₂(H₂O)], and the Mannich base (Scheme 1), three complexes have been obtained: [Co₂(L)₂(hfac)₂] (**1**), [Ni₂(L)₂(hfac)₂] (**2**), and [Cu(L)(hfac)] (**3**).

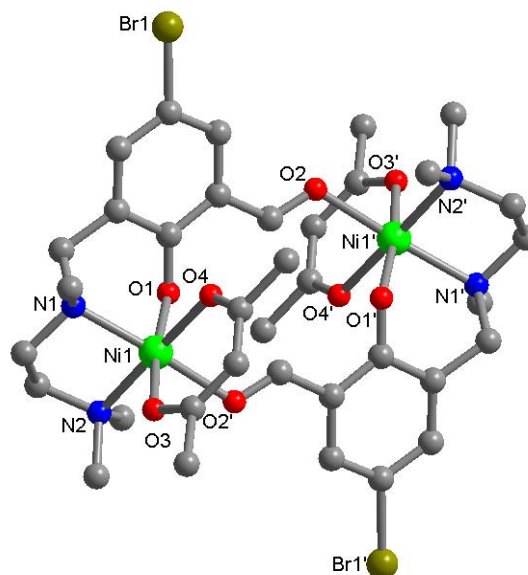


Scheme 1 – Structure of the Mannich base, HL.

Description of the crystal structures of 1 - 3

Compounds **1** and **2** are isostructural, crystallizing in the $P-1$ triclinic space group, therefore we describe here only the nickel derivative, of **2**. Its structure consists of centrosymmetric binuclear species resulted from two {Ni(L)(hfac)} units which are coordinated to each other by the carbonyl groups (Figure 1). The nickel atoms show an octahedral geometry with the basal plane formed by three oxygen atoms (a phenoxido- oxygen atom, a carbonyl- one from the Mannich ligand, and an oxygen atom from the hfac⁻ ligand) as well as by a nitrogen atom, having the distances: N(2) – Ni(1) = 2.096(9), O(1) – Ni(1) = 2.034(8), O(2)' – Ni(1) = 2.098(7) and O(3) – Ni(1) = 2.064(8) Å (*symmetry code*: (') = $-x + 2, -y + 1, -z$). The apical positions are occupied by a nitrogen atom of the Mannich base and by an oxygen atom arising from the β -diketonato

ligand (O(4) – Ni(1) = 2.045(7) and N(1) – Ni(1) = 2.100(9) Å). The intramolecular distance between the metal ions is 6.535 Å. The unit cell parameters for compound **1** are: $a = 9.295(2)$ Å, $b = 11.186(3)$ Å, $c = 11.962(3)$, $\alpha = 80.64(2)^\circ$, $\beta = 68.31(2)^\circ$, $\gamma = 84.90(2)^\circ$, and $V = 1139.73$ Å³.

Fig. 1 – Perspective view of compound **2** with the atom numbering scheme. Hydrogen and fluorine atoms have been omitted for clarity (') = $-x + 2, -y + 1, -z$.

The mononuclear complex **3** crystallizes in $P-1$ triclinic space group. Its structure is shown in Figure 2. During the synthesis, the β -diketonato precursor, [Cu(hfac)₂(H₂O)], loses one hfac⁻ group and the water molecule. The deprotonated Mannich base acts as a chelating ligand towards the metal ion. The copper ion shows a coordination number of five, with a slightly distorted square pyramidal geometry. The trigonal distortion from the square pyramidal geometry is evaluated by the τ parameter, defined as $\tau = [(\theta - \phi)/60]$,¹⁰ where θ and ϕ are the largest and second-largest angles between the donor atoms forming the basal plane in square-pyramidal geometry ($\theta > \phi$). The value of the parameter for Cu(1) is then 0.050. The base plane is described by two nitrogen atoms and an

oxygen from the Mannich base and by one oxygen provided by the hfac⁻ ligand: N(1) – Cu(1) = 2.021(8), N(2) – Cu(1) = 2.001(10), O(1) – Cu(1) = 1.871(8) and O(3) – Cu(1) = 1.998(7) Å. The second oxygen atom from the hfac⁻ ligand is shown in the apical position (Cu(1) – O(4) = 2.228(9) Å).

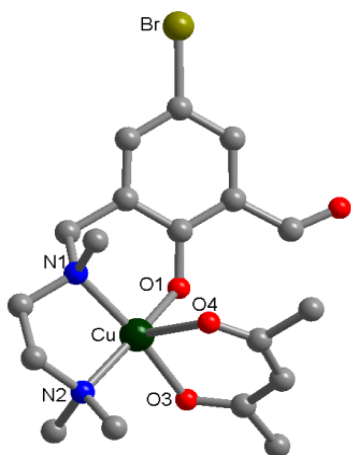


Fig. 2 – Structure of compound **3** with the atom numbering scheme. Hydrogen and fluorine atoms have been omitted for clarity.

Selected bond lengths and angles for compounds **2** and **3** are collected in Table 2.

Spectral properties

In the FTIR spectra of compounds **1** - **3**, the characteristic band for the C=O group is observed

at 1650(vs), 1652(vs) and 1676(vs) cm⁻¹, respectively. The bands due to the -CF₃ groups are observed at 1145(vs) and 1148(vs) cm⁻¹. The diffuse reflectance spectrum of **2** (Figure 3) shows the characteristic features for (pseudo)octahedral Ni(II) complexes, with two bands at 1040 and 631 nm assigned to ³A₂→³T₂ (ν₁) and ³A₂→³T₁ (ν₂) transitions, respectively (assuming the *O* symmetry for the two nickel ions). The weak band at 791 nm is assigned to the spin forbidden transition ³A₂→¹E. The shoulder at ~420 nm could be assigned to the ³A₂→³T₁(P) (ν₃) transition of Ni(II). The value of the 10Dq parameter is given by the energy of the ν₁ transition (9596 cm⁻¹) and the value of the Racach parameter, *B*, is calculated using König's equations,¹¹ *B* = 880 cm⁻¹. Consequently, the parameter of the nephelauxetic series is β = 0.847. The UV-VIS-NIR spectrum of **1** shows a band with a maximum at 1112 nm, ascribed to the ⁴T₁→⁴T₂ transition of the hexacoordinated Co(II) ion (assuming the *O* symmetry). The other *d-d* transitions are covered by the CT and ligands absorption bands. Compound **3** presents an asymmetric band (~686 nm) with a tail towards low energies, which is characteristic for square-pyramidal Cu(II) complexes.

In conclusion, we have illustrated with new examples that hexafluoroacetylacetonato complexes are useful starting materials in designing mixed ligand complexes.

Table 2

Selected bond lengths (Å) and angles (°) for **2** and **3**

2	3
<i>bond lengths (Å)</i>	
N(1) - Ni(1) = 2.100(9)	N(1) - Cu(1) = 2.021(8)
N(2) - Ni(1) = 2.096(9)	N(2) - Cu(1) = 2.001(10)
O(1) - Ni(1) = 2.034(8)	O(1) - Cu(1) = 1.871(8)
O(2)' - Ni(1) = 2.098(7)	O(3) - Cu(1) = 1.998(7)
O(3) - Ni(1) = 2.064(8)	O(4) - Cu(1) = 2.234(8)
O(4) - Ni(1) = 2.045(7)	N(1) - Cu(1) = 2.021(8)
<i>angles (°)</i>	
O(1) - Ni(1) - O(2)' = 89.2(3)	O(1) - Cu(1) - O(3) = 85.6(3)
O(1) - Ni(1) - O(3) = 173.0(3)	O(1) - Cu(1) - O(4) = 91.9(3)
O(1) - Ni(1) - O(4) = 87.9(3)	O(1) - Cu(1) - N(1) = 93.8(3)
O(1) - Ni(1) - N(1) = 89.8(3)	O(1) - Cu(1) - N(2) = 167.2(3)
O(1) - Ni(1) - N(2) = 94.2(3)	O(3) - Cu(1) - O(4) = 88.3(3)
O(2)' - Ni(1) - O(3) = 87.2(3)	O(3) - Cu(1) - N(1) = 170.0(3)
O(2)' - Ni(1) - O(4) = 90.5(3)	O(3) - Cu(1) - N(2) = 90.5(3)
O(2)' - Ni(1) - N(1) = 175.7(3)	O(4) - Cu(1) - N(1) = 101.7(3)
O(2)' - Ni(1) - N(2) = 89.5(3)	O(4) - Cu(1) - N(2) = 100.2(4)
O(3) - Ni(1) - O(4) = 86.2(3)	N(1) - Cu(1) - N(2) = 87.9(3)
O(3) - Ni(1) - N(1) = 94.2(3)	

Table 2 (continued)

O(3) - Ni(1) - N(2) = 91.7(3)

O(4) - Ni(1) - N(1) = 93.7(3)

O(4) - Ni(1) - N(2) = 177.9(3)

N(1) - Ni(1) - N(2) = 86.4(4)

symmetry code: (') = -x + 2, -y + 1, -z

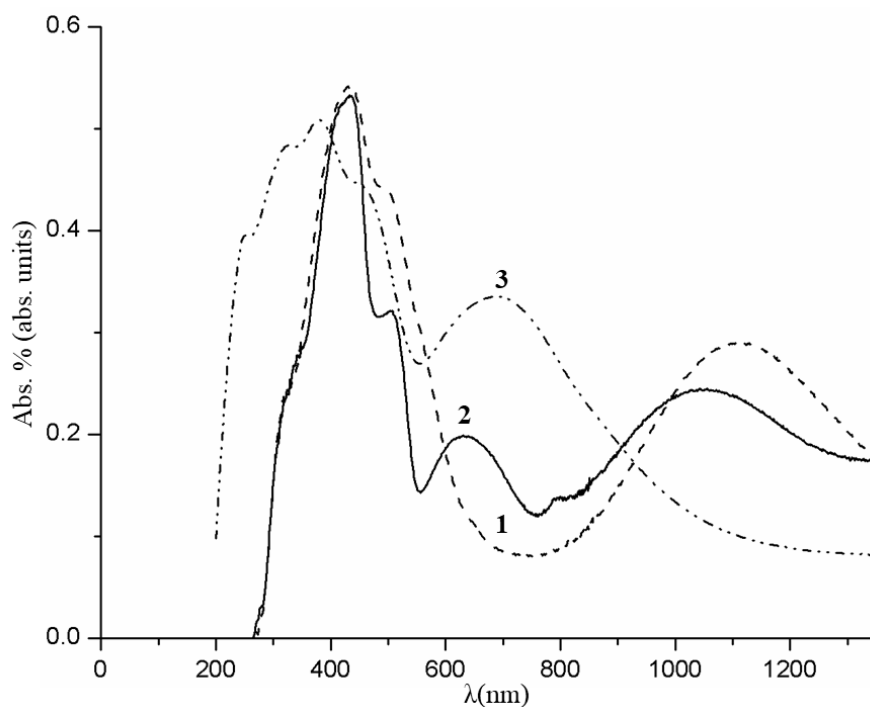


Fig. 3 – UV-Vis-NIR spectra for complexes 1-3.

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