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Mirela Călinescu* [a] & Ana Emandi [a]

[a] Department of Inorganic Chemistry, University of Bucharest, Bucharest, Romania

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METAL COMPLEX MONOMERS OF CU(II) AND NI(II) WITH ALLYLACETOACETATE AND 2-HYDRAZINOBENZOTHIAZOLE

Mirela Călinescu and Ana Emandi*
Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Rosie, Bucharest, Romania

Metal complexes of Cu(II) and Ni(II) with allylacetoacetate (allylH) and 2-hydrazinobenzothiazole (hydrH) as ligands were prepared and characterized on the basis of elemental and thermogravimetric analyses, magnetic susceptibility measurements, infrared and ultraviolet-visible spectra. The presence of Cu^{2+} favors the condensation of a carbonyl group of allylacetoacetate with amine group of the hydrazide (a template reaction). Using the copper(II) acetate, a dimeric complex [Cu_2(allylhydrH)$_2$($CH_3COO)_2$] was obtained, while copper(II) chloride gives a monomeric complex [Cu(allylhydrH)(H_2O)Cl]. The cation Ni^{2+} does not favor the condensation, and the resulted compounds are the mononuclear coordinative compounds having the formulas: [Ni(allyl)(hydrH)(H_2O)Cl] and [Ni(allyl)(hydrH)$_2$]Cl.

1. INTRODUCTION

A survey of the literature data shows that the stabilization of the polymers is achieved by two general methods: a) the use of the additives and b) the modification of the molecular structure [1,2]. This latter method is used when the initiation rate is high and the additives are then less effective.

Thus, several coordination polymers were prepared from organic polymers containing the functional groups which can bind metal ions [3–5].

Since the composition of such a metal complex polymer is not always homogeneous, we tried to obtain complex compounds which may act as monomers for preparation of the metal complex copolymers.

In this work we have focused our attempts on the preparation and the characterization of the four complex compounds of Ni(II) and Cu(II) with allylacetoacetate (allylH) and 2-hydrazinobenzothiazole (hydrH) as ligands.

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*Corresponding author. E-mail: mirela_calinescu@hotmail.com

These metal complexes have one or more an unsaturated allyl group which can undergo copolymerization, while the electronic delocalization on benzothiazole moiety improves the optical properties of the copolymers.

2. EXPERIMENTAL

All the chemicals used were of analytical reagent grade. Allylacetoacetate, 98%, d = 1,04 g/cm^3 (Merck), mercaptobenzothiazole (Merck) and hydrazine hydrate, 80%, d = 1,03 g/cm^3 (Merck) were used without purification.

The preparation of 2-hydrazinobenzothiazole was made according to the literature method [6], by the condensation of mercaptobenzothiazole with hydrazine, in ethanol. M.p. = 199°C.

Preparation of the Complexes

[Cu_2(allylhydrH)$_2$($CH_3COO)_2$] **(1)**. Allylacetoacetate (6.8 ml; 0.05 mol) was added to a solution of 2-hydrazinobenzothiazole (8.25 g; 0.05 mol) in ethanol. No change is observed after stirring at room temperature for 30 minutes. By adding to this mixture an ethanolic solution of $Cu(CH_3COO)_2 \cdot H_2O$ (10 g; 0.05 mol), a brown precipitate was formed immediately. It was filtered, washed with ethanol and dried in air. The complex is insoluble in common organic solvents.

[Cu(allylhydrH)(H_2O)Cl] **(2)**. This compound was obtained by a similar method, using in this case $CuCl_2 \cdot 2H_2O$ (8.55 g; 0.05 mol) for the same quantities of allylacetoacetate and 2-hydrazinobenzothiazole. The complex, dark-green coloured, is soluble in acetonitrile.

[Ni(allyl)(hydrH)(H_2O)Cl] **(3)**. The complex was prepared by mixing an ethanolic solution of 2-hydrazinobenzothiazole (8.25 g; 0.05 mol) with allylacetoacetate (6.8 ml; 0.05 mol) and an ethanolic solution of $NiCl_2 \cdot 6H_2O$ O (12 g; 0.05 mol). The resulting solution was digested at room temperature for about one hour. The light-green compound thus obtained was filtered, washed with ethanol and dried in air.

[Ni(allyl)(hydrH)$_2$]Cl **(4)**. was similarly prepared, but in 1:2:1 molar ratio of allylacetoacetate:2-hydrazinobenzothiazole:Ni(II) chloride. A light-blue compound was obtained. The Ni(II) complexes are soluble in ethanol.

The purity of the complexes was determined by C, H analyses. The metal content was determined by standard procedures [7].

Physical measurements. Infrared spectra (in KBr pellets) were recorded on an IR BIORAD FTS 135 spectrophotometer, in the range of 4000–400 cm^{-1}. Diffuse reflectance spectra were measured on a Specord

M-40 spectrophotometer in the range of 200–900 nm. Thermogravimetric analyses were carried out in static air atmosphere, at a heating rate of 10°C/min, using a MOM Q-1500 derivatograph. Magnetic susceptibility measurements were performed by the Faraday method at room temperature using $Hg[Co(SCN)_4]$ as a calibrant.

3. RESULTS AND DISCUSSION

The analytical data for the complex compounds are shown in (Table 1) and the significant bands of 2-hydrazinobenzothiazole and its complexes observed in the infrared spectra are listed in (Table 2).

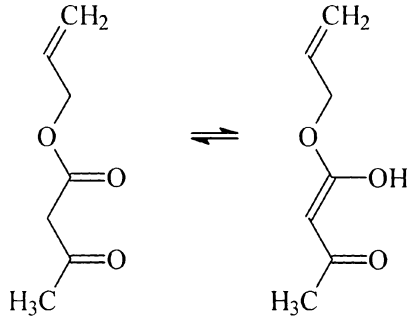
It is known that allylacetoacetate exists in two tautomeric forms both in the keto form (I) and in the enolic form (II) (Fig. 1), the ratio of this latter form (II) being about 80%. In the enolic form allylacetoacetate can coordinate through the carbonylic and the enolic oxygen atoms.

TABLE 1 Analytical Data for the Complex Compounds

	C%		H%		Metal%	
Complex	Calc.	exp.	Calc.	exp.	Calc.	exp.
1. $[Cu_2(allylhydrH)_2(CH_3COO)_2]$	46.77	46.32	4.14	4.02	15.46	15.32
2. $[Cu(allylhydrH)(H_2O)Cl]$	41.48	41.08	3.95	3.85	15.67	15.50
3. $[Ni(allyl)(hydrH)(H_2O)Cl]$	41.63	41.23	4.70	4.80	14.62	14.41
4. $[Ni(allyl)(hydrH)_2]Cl$	44.48	44.10	4.23	4.10	10.41	10.32

TABLE 2 Characteristic Bands in the IR Spectra of 2-hydrazinobenzothiazole and the Metal Complexes (ν_{max}, cm^{-1})

Assignments	hydrH	**1**	**2**	**3**	**4**
$\nu(NH_2)$ as	3436 m	–	–	3400 i	3413 m
$\nu(NH_2)$ sim	3317 mi	–	–	3280 i	3258 i
ν(NH) sec	3200 m	3180 m	3204 i	3187 i	3156 i
$\delta(NH_2)$	1649 i	–	–	1626 i	1628 i
ν(C = N) endo	1594 mi	1589 m	1588 m	1589 mi	1589 mi
exo		1629 mi	1614 mi	–	–
ν(C = O)	–	–	–	1626 i	1628 i
$\nu(OH)(H_2O)$	–	–	3438 m	3400 i	–
$\nu(CH_3COO)$	–	1736 mi	–	–	–



(I) (II)

FIGURE 1 Keto form (I) and enolic form (II) of allylacetoacetate.

Moreover, the carbonylic group can react with amine group of 2-hydrazinobenzothiazole (hydrH) to provide a hydrazone Schiff base very easy in the presence of a metallic cation. Our attempts to obtain a hydrazone ligand *in situ* with in the presence of a metal cation was possible only for Cu^{2+}.

This is the reason why in the IR spectra of the *copper(II)* complexes the bands assigned to asymmetric and symmetric N-H stretching mode of NH_2 group of 2-hydrazinobenzothiazole, at 3436 and 3317 cm^{-1} [8] are not observed.

Instead of a band at 1650–1690 cm^{-1} due to the $>C=O$ stretching frequency in allylacetoacetate moiety, the IR spectra of these complexes exhibit another bands, at 1629 cm^{-1} (**1**) and 1614 cm^{-1} (**2**), assignable to the stretching vibration of $>C=N$ group formed by condensation [9–13]. The bands due to $\nu(C=N)$ endocyclic of benzothiazole moiety at 1594 cm^{-1} [14] shows a negative shift in the spectra of the Cu(II) complexes. No bands assigned to the vibration ν(OH) of the enolic group in allylacetoacetate are observed in the case of these complexes, indicating that the deprotonation of the OH group has been take place during the complexation.

A hydrazone compound has been obtained by the condensation between the carbonyl group of allylacetoacetate and the amine group of 2-hydrazinobenzothiazole. This hydrazone ligand coordinates to the copper(II) ion through the two azomethinic nitrogen atoms of (hydrH) and the enolic oxygen of (allylH) .

For the complex (**2**), the broad medium band which exhibits at 3442 cm^{-1} is due to the ν(OH) of coordinated water [15].

The IR spectra of *nickel(II)* complexes present all the bands due to NH_2 group. It can be concluded that the condensation reaction of allylacetoacetate

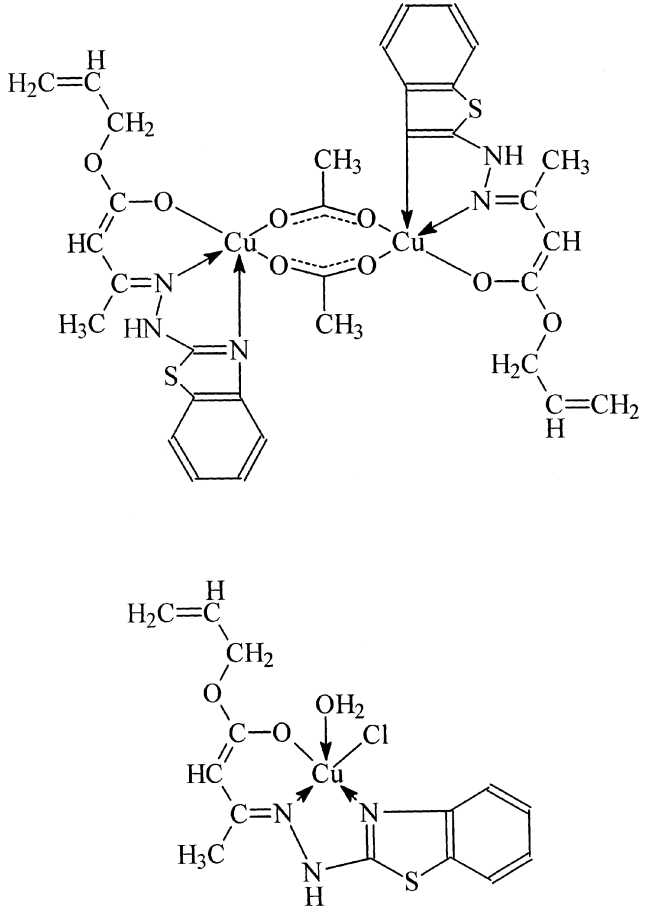


FIGURE 2 Suggested structures for $[Cu_2(allylhydrH)_2(CH_3COO)_2]$ and $[Ni(allyl)(hydrH)_2]Cl$ $[Cu(allylhydrH)(H_2O)Cl]$.

with 2-hydrazinobenzothiazole does not take place and the coordinative compounds with mixed ligands were obtained.

The negative shifts for these bands and for the bands due to $\nu(C = N)$ endocyclic have observed and they showed the coordination of 2-hydrazinobenzothiazole through the nitrogen atoms of the amine and the azomethine groups.

The stretching frequency of carbonylic group, $\nu(C = O)$, appears at 1626–1628 cm^{-1} and they are overlaped by the frequency of the $\delta(NH_2)$ group. The bands due to the stretching vibration of the enolic OH group dissapear in the IR spectra of the complexes. It can be supposed that

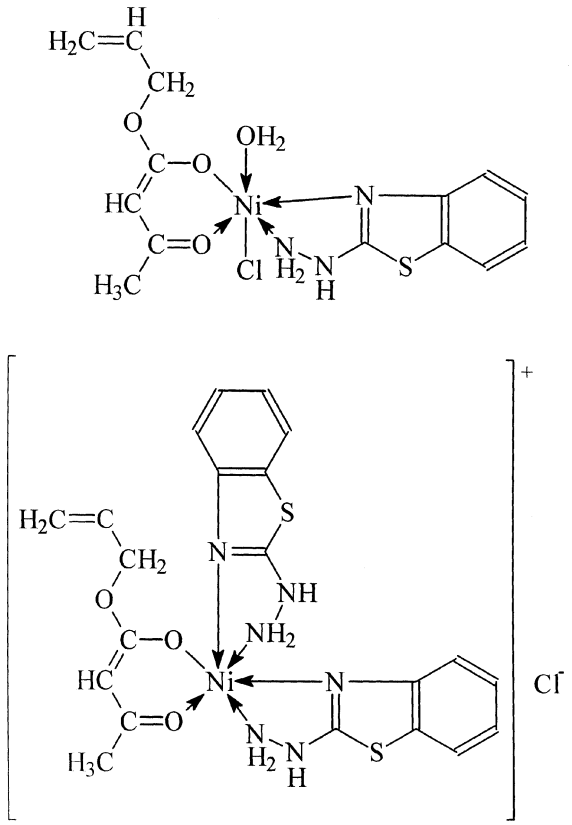


FIGURE 3 Suggested structures for [Ni(allyl)(hydrH)(H_2O)Cl] and [Ni(allyl)-(hydrH)$_2$]Cl.

allylacetoacetate is linked to Ni(II) cation through the carbonylic and the enolic oxygen atoms.

The new band observed at around 3400 cm^{-1} in the IR spectrum of the complex (**3**) may be assigned to coordinated water according to the literature data [15].

The presence of the coordinated water in the complexes [Cu(allyl-hydrH)(H_2O)Cl] and [Ni(allyl)(hydrH)(H_2O)Cl] is also supported by the thermogravimetric analyses. The thermogravimetric curves of these two compounds show exothermic peaks in the range 130–150°C (complex **2**) and 140–200°C (complex **3**), which correspond to the loss of the coordinated water [16]. The endothermic processes, observed in the range 220–300°C for the complexes **2**, **3** and **4** correspond to the loss of the

coordinated or anionic chlorine [17]. All the complexes lose the organic ligands in the large exothermic processes, in the range 300–700°C.

According with the above results, the following formulas were proposed for the complex compounds (Figs. 2 and 3):

Magnetic and Electronic Spectral Data

The *copper(II)* complexes show the magnetic moments very close to the spin-only value corresponding to one unpaired electron [18]: 1,83 BM (complex **1**) and respectively 1,78 BM (complex **2**).

The electronic spectra of these complexes are very similar and exhibit two absorption bands: the first broad band over the range 15000–16000 cm^{-1} and the second around 21000 cm^{-1}. These agree with a five-coordinate square pyramidal stereochemistry [19,20]. Taking into account this assumption in (Table 3) are presented the assignments of the observed bands.

The values of the magnetic moments of the nickel(II) complexes 3,04 BM (complex **1**) and 3,14 BM (complex **2**) correspond to an octahedral geometry [21] around Ni(II) cation.

Due to the low symmetry of the ligand field in the electronic spectrum of [Ni(allyl)(hydrH)(H_2O)Cl] a splitting of the "octahedral" bands are

TABLE 3 Electronic Transitions for Copper(II) Complexes

Observed bands (ν_{max}, cm^{-1})		
Complex **1**	Complex **2**	Assignments
16130	15600	$xy \rightarrow x^2\text{-}y^2$
21276	21000	$xz,yz \rightarrow x^2\text{-}y^2$

TABLE 4 Electronic Transitions for [Ni(allyl)(hydrH)(H_2O)Cl]

Observed bands (ν_{max},cm^{-1})	Assignments
9520	$^3B_1 \rightarrow {}^3A_1$ ($^3T_2$)
11100	$^3B_1 \rightarrow {}^3B_2$, $^3A_2$ ($^3T_2$)
12500	$^3B_1 \rightarrow {}^1A_1$, $^1B_1$ (^1D)
15625	$^3B_1 \rightarrow {}^3B_2$ ($^3T_1$)
16950	$^3B_1 \rightarrow {}^3B_1$, $^3A_2$ ($^3T_1$)
23250	$^3B_1 \rightarrow {}^1A_1$, ($^1D$)
26300	$^3B_1 \rightarrow {}^3A_2$ ($^3T_1$, P)

TABLE 5 Electronic Transitions for [Ni(allyl)(hydrH)$_2$]Cl

Observed bands (ν_{max},cm^{-1})	Assignments
10200	$^3A_2 \rightarrow {}^3E$ ($^3T_{2g}$)
10900	$^3A_2 \rightarrow {}^3A_1$ ($^3T_{2g}$)
14285	$^3A_2 \rightarrow {}^3E$ ($^3T_{1g}$)
15625	$^3A_2 \rightarrow {}^3A_2$ ($^3T_{1g}$)
21275	$^3A_2 \rightarrow {}^3E$ ($^3T_{1g}$, P)
26300	$^3A_2 \rightarrow {}^3A_2$ ($^3T_{1g}$, P)

observed. The position and the intensity of these bands are in according to a trans-C_{2v} symmetry of this complexes [22] and the assignments of the absorption maxima observed in the visible-ultraviolet region of this complex are showed in the (Table 4).

The electronic spectrum of the [Ni(allyl)(hydrH)$_2$]Cl complex, reveals a distorted hexacoordinated symmetry around the Ni(II) cation, the most probably C_{3v} [22]. The assignments of the observed bands are listed in the (Table 5).

CONCLUSIONS

A series of the new four metal complex monomers of Cu(II) and Ni(II) cations with allylacetoacetate (allylH) and 2-hydrazinobenzothiazole (hydrH) as ligands have been obtained by means of the controlled reactions. The experimental data showed that a template rections were possible only for Cu(II) cation, where the nature of the inorganic salt of Cu(II) was a decisive factor in obtaining a dinunuclear complex **(1)** by using $Cu(CH_3COO)_2 \cdot H_2O$ and a mononuclear complex **(2)** by using $CuCl_2.2H_2O$. The coordinative compounds of Ni(II) cation have been separated only as a mononuclear mixed ligands coordinative compounds. The type of these coordinative compound depends only on the stoichiometric ratio Ni / (hydrH) / (allylH); a ratio of 1/1/1 in the complex **(3)** and a ratio of 1/2/1 in the complex **(4)**. All of these compounds are very stabile at the room temperature and the normal pressure and they are available in obtaining the different nanostructured metal complex copolymers with intersting optical properties.

REFERENCES

[1] Gad, A. M., El-Dissouky, A., Mansour, E. M., & El-Maghraby, A. (2000). *Polym. Degrad. Stab.*, *68*, 153.

[2] Diab, M. A., El-Sonbati, A. Z., El-Sonbari, A. A., & Taha, F. I. (1989). *Polym. Degrad. Stab.*, *24*, 51.

[3] El-Sonbati, A. Z. & Diab, M. A. (1988). *Acta Polym.*, *39*, 558.
[4] El-Sonbati, A. Z., El-Dissouky, A., & Diab, M. A. (1989). *Acta Polym.*, *40*, 112.
[5] Gad, A. M., El-Dissouky, A., & Alim Abdel, W. (1995). *Polym. Degrad. Stab.*, *50*, 163.
[6] Katz, L. (1951). *J. Amer. Chem. Soc.*, *73*, 4007.
[7] Macarovici, C. G. (Ed.). (1975). *Quantitative Inorganic Chemical Analysis*, Academia Republicii Socialiste România: Bucharest, p. 222, 350, 352.
[8] Campbell, M. J. M. (1975). *Coordin. Chem. Rev.*, *15*, 279.
[9] Aggarwal, R. C. & Rao, T. R. (1978). *J. Inorg. Nucl. Chem.*, *40*, 171.
[10] Goyal, S. & Lal, K. (1990). *Acta Chim. Hung.*, *127*(3), 353.
[11] Mohan, M., Kumar, A., & Kumar, M. (1987). *Inorg. Chim. Acta*, *136*, 65.
[12] Mohan, M., Gupta, N. K., & Kumar, M. (1992). *Inorg. Chim. Acta*, *197*, 39.
[13] Sharma, R. C., Ambwani, J., & Varshney, V. K. (1992). *J. Indian Chem. Soc.*, *69*, 770.
[14] Şumalan, L., Macarovici, D., Neamţu, M., & Coman, M. (1997). *Rev. Roum. Chim.*, *42*(4), 277.
[15] Nakamoto, K. (Ed.). (1963). *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley: New York, N.Y., USA, p.156.
[16] Lukic, S. R., Petrovic, D. M., & Petrovic, A. F. (1988). *J. Therm. Anal.*, *34*, 1015.
[17] Tossidis, I. A., Bolos, C. A., & Cristofides, A. (1989). *J. Therm. Anal.*, *35*, 1339.
[18] Mohan, M., Kumar, A., & Kumar, M. (1987). *Inorg. Chim. Acta*, *136*, 65.
[19] Mohan, M., Gupta, M. P., Chandra, L., & Jha, N. K. (1988). *Inorg. Chim. Acta*, *151*, 61.
[20] Abragam, A. & Bleaney, B. (Ed.). (1970). *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press: London, p. 448, 449.
[21] Dutta, R. L. & Hossain, M. Md. (1985). *J. Sci. Ind. Res.*, *44*, 635.
[22] Lever, A. B. P. (Ed.). (1984). *Inorganic Electronic Spectroscopy (second edition)*, Elsevier Amsterdam-Oxford-New York: Tokyo, p. 516–520.