

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

TWO NEW HYDROGEN BONDED NETWORKS OBTAINED IN $MCl_2 \cdot xH_2O$ ($M = Mn, Cu$)- N,N' -ETHYLENEBISACETAMIDE SYSTEM

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The paper presents the synthesis and characterization by electrical conductivity measurements, UV-Vis and FTIR spectra of two new chemical species obtained in $MCl_2 \cdot xH_2O$ ($M = Cu, x=2$; $M = Mn, x=4$)- N,N' -ethylenebisacetamide (EBA) – ethanol system. The X-ray structural analysis of two compounds – inorganic-organic cocrystals comprising of neutral 1D-inorganic polymeric chains $\{MCl_2(H_2O)_2\}_n$ ($M=Cu(II), Mn(II)$), N,N' -ethylenebisacetamide (EBA) molecules and solvent ethanol molecules (**1** and **2** respectively). Although the composition of cocrystals is very similar $MCl_2(H_2O)_2 \cdot EBA \cdot 0.5C_2H_5OH$ and differs only by metal (copper or manganese) they crystallize in different space groups. The copper(II) and manganese(II) ions have distorted octahedral surrounding completed by four chlorine atoms and two water molecules. The octahedrons form one-dimensional chains by Cl – Cl edge sharing. Organic molecules connect these chains in 3D- channel network via O–H \cdots O and N–H \cdots Cl hydrogen bonds.

INTRODUCTION

Crystalline hydrogen bonded assemblies of neutral pure inorganic and organic components are of current interest because these systems allow to create new compositions of matter with desirable properties by replacement of only one component (inorganic or organic) and permanent second component. Most of the inorganic-organic hybrid structures¹⁻⁴ are composed of inorganic anions like $[ZnCl_4]^{2-}$, $[Cd_2Cl_8]^{4-}$, $[Cu_3Cl_8(H_2O)_2]^{2-}$, $[CoCl_4]^{2-}$ and organic cations like bis(*p*-toluidinium), 2-(3-pyridin)benzimidazolium and 1,6-hexamethylenediammonium. Another type of inorganic-organic structures are hydrogen bonded networks formed by hydrated metal halide polymers and organic compounds containing O and N atoms

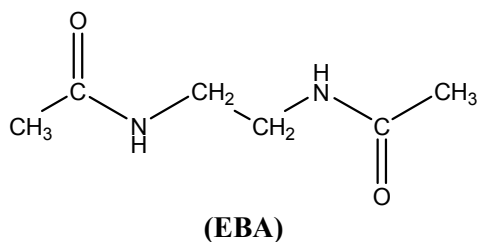
capable to establish H bonds⁵⁻⁹. Inorganic-organic assemblies can be classified in two types. The first type contains compounds which forms salts through hydrogen transfer and the second type refers to cocrystals which are stabilized by weak interactions^{10,11} (hydrogen bond, van der Waals etc.).

Inorganic-organic supramolecular assemblies are versatile compounds which can be used in preparing structures with similar properties to metal-organic frameworks (MOFs), for example hydrogen storage, catalytic properties etc. In the literature¹²⁻¹⁴, the magnetic and optical properties are discussed related to compound with molecular formula $[MCl_2 \cdot nH_2O]$, where M(II) is a first-row transition metal.

This paper deals with the synthesis and characterization of two new inorganic-organic assemblies

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obtained in the systems: $MCl_2 \cdot xH_2O$ ($M = Cu$, $x=2$; $M = Mn$, $x=4$) – (EBA) – ethanol.



Herein, we present the synthesis and the crystal structure of two inorganic-organic cocrystals comprising of neutral 1D-inorganic polymeric chains $\{MCl_2(H_2O)_2\}_n$ ($M = Cu(II)$, $Mn(II)$), *N,N'*-ethylenebisacetamide (EBA) molecules and solvent ethanol molecules – $MCl_2(H_2O)_2 \cdot EBA \cdot 0.5C_2H_5OH$ ($M = Cu(II)$, $Mn(II)$) – **1** and **2** respectively.

RESULTS AND DISCUSSION

In the literature are described coordination compounds of ethylene bis(acetamide) (EBA) and derivatives with first row transition metals¹⁵⁻¹⁷ like $Co(II)$, $Mn(II)$, $Ni(II)$. The coordination takes place through the O atom from EBA or derivatives. Cambridge Crystallographic Data Centre¹⁸ contains only data related to a complex compound of $Co(II)$ with EBA, catena-(bis(μ_2 -*N,N'*-Diacetyl-1,2-ethanediamine)-diaqua-cobalt(II) dibromide.¹⁵ It has been established that two Co atoms are coordinating the bidentate ligand EBA. The values of charge densities obtained in Molecular modeling (Fig. 1) of *N,N'*-ethylene bisacetamide (performed using molecular mechanics

method MM+; Semi-empirical method MNDO; Molecular mechanics optimization-Steepest Descent) indicate the most probable coordination sites – the N and the O atoms.

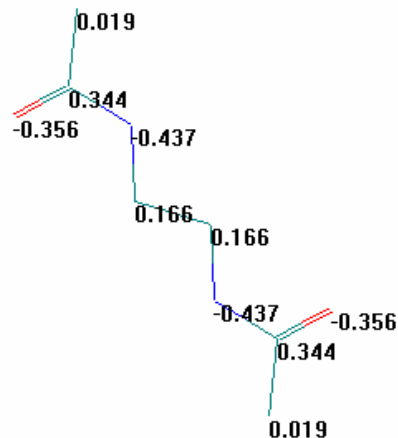


Fig. 1 – Molecular modeling for EBA; C-green; N-blue; O-red; charge densities shown.

Contrary to our expectations in the systems studied we obtained two hybrid inorganic- organic three-dimensional frameworks stabilized by hydrogen bonds.

Description of the structure

Compounds **1** and **2** contain the inorganic layer $MCl_2(H_2O)_2$ ($M = Cu$, Mn respectively) and the organic layer EBA molecules, along with ethanol molecules (solvent). The structures of **1** and **2** are presented in fig. 2 (a, b).

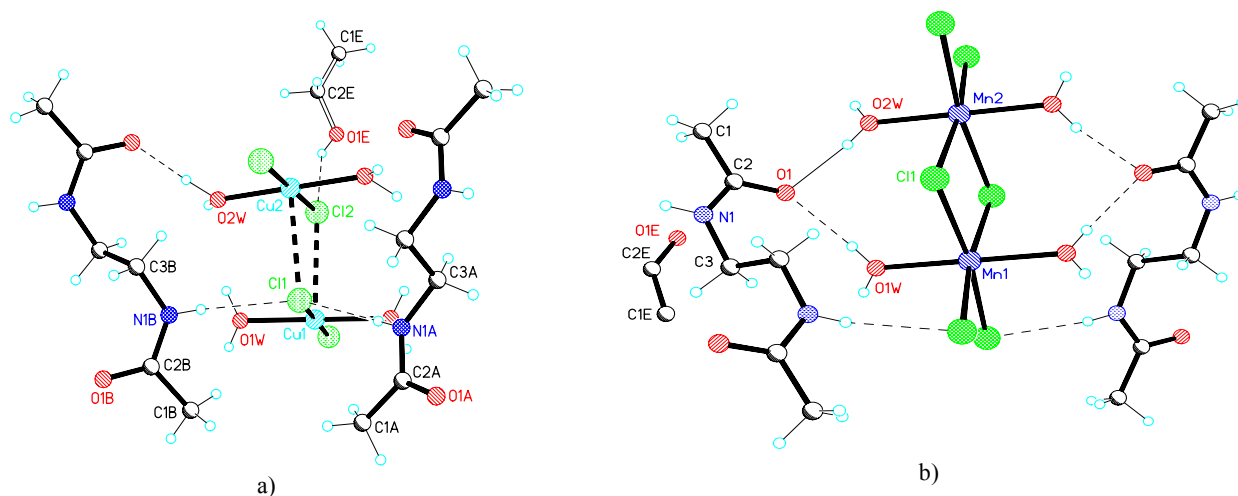


Fig. 2 (a,b) – View of the compounds **1** and **2** with the crystallographic numbering scheme.

Although the composition of cocrystals is very similar $MCl_2(H_2O)_2$ -EBA-0.5 C_2H_5OH and differs only by metal (copper or manganese) they crystallize in different space groups (Table 1).

The inorganic components $MCl_2(H_2O)_2$ of **1** and **2** have practically similar structures including

the coordination polyhedron sharing an edge, giving rise to the polymer chains $\{MCl_2(H_2O)_2\}_n$, Fig. 3 (a,b).

Table 1

Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$C_7 H_{19} Cl_2 Cu N_2 O_{4.50}$	$C_7 H_{19} Cl_2 Mn N_2 O_{4.50}$
Formula weight	337.68	329.08
<i>T</i> , (K)	153(2)	153(2)
Wavelength, (Å)	0.71073	0.71073
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$	orthorhombic, <i>Pbn</i>
Unit cell dimensions		
<i>a</i> , (Å)	7.586(2)	12.410(3)
<i>b</i> , (Å)	9.447(2)	15.240(3)
<i>c</i> , (Å)	9.968(2)	7.570(2)
α , (deg)	102.82(3)	90
β , (deg)	96.40(3)	90
γ , (deg)	94.04(3)	90
<i>V</i> , (Å ³)	688.9(2)	1431.7(5)
<i>Z</i> , <i>d_c</i> , (g/cm ³)	2, 1.628	4, 1.527
μ , (mm ⁻¹)	1.978	1.300
<i>F</i> (000)	348	680
Crystal size, (mm)	0.2 x 0.15 x 0.15	0.15 x 0.15 x 0.10
θ range for data collection, (deg)	3.22 to 27.00	2.67 to 26.00
Limiting indices	$-9 \leq h \leq 9, -12 \leq k \leq 12,$ $-12 \leq l \leq 12$	$-15 \leq h \leq 15, -12 \leq k \leq 18,$ $-7 \leq l \leq 9$
Reflections collected / unique	28166 / 2988 [<i>R</i> (int) = 0.0484]	3997 / 1415 [<i>R</i> (int) = 0.0142]
Completeness to $\theta = 27.00$, %		99.9
Refinement method		Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2988 / 2 / 169	1415 / 2 / 90
Goodness-of-fit on <i>F</i> ²	1.091	1.018
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0363, <i>wR</i> 2 = 0.1140	<i>R</i> 1 = 0.0263, <i>wR</i> 2 = 0.0951
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0380, <i>wR</i> 2 = 0.1148	<i>R</i> 1 = 0.0373, <i>wR</i> 2 = 0.1013
Largest diff. peak and hole, (e Å ⁻³)	1.148 and -0.324	0.451 and -0.412 e.Å ⁻³

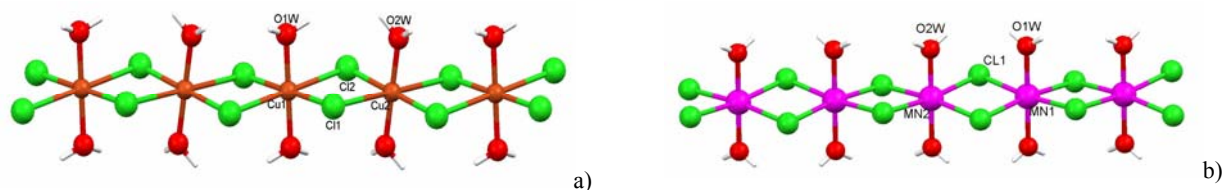


Fig. 3 (a,b) – View of the chains of Cu(II) and Mn(II) .

Two crystallographic independent atoms Mn(1) and Mn(2) which belong to the inorganic polymer $\{MnCl_2(H_2O)_2\}_n$ (**2**) share an edge from the coordination polyhedron of the metals Fig. 3a. The metal ions are linked by the μ -chlorine atoms. Interatomic distance between two Mn atoms from neighboring units of the polymeric chain is 3.785 Å. The coordination polyhedron of the metal is a distorted octahedron with D_{2h} symmetry, the metal being surrounded by four chlorine atoms and two

water molecules. Interatomic distances are Mn–Cl 2.5592(6) Å, Mn–O(1W) 2.165(2) Å for Mn(1) and 2.5876(6), 2.112(2) Å for Mn(2) (Table 2).

Packing of the structure along *c* axis shows the polymer chains $\{MnCl_2(H_2O)_2\}_n$ surrounded by EBA molecules, Fig.4, b.

Among the compounds found in Cambridge Structural Database¹⁸ one has the most resembling structure with **2**¹⁹. These structures are composed of almost the same polymeric chain with similar

coordination polyhedron and the difference consists of the structure of the organic molecules interacting with the inorganic layers, $\{\text{MnCl}_2(\text{H}_2\text{O})_2\}_n$. Thus, inorganic layers interact

with a positively charged specie, trimethylammonium cation¹⁹ and in our case EBA is a neutral organic molecule.

Table 2

Bond lengths (Å) and angles (deg) for **1** and **2**

Compound 1		Compound 2	
Cu(1)–Cl(1)	2.297(1)	Mn(1)–Cl(1)	2.5592(6)
Cu(1)–Cl(2)	2.845(1)	Mn(1)–O(1W)	2.165(2)
Cu(1)–O(1W)	1.981(2)	Mn(2)–Cl(1)	2.5876(6)
Cu(2)–Cl(2)	2.298(1)	Mn(2)–O(2W)	2.112(2)
Cu(2)–Cl(1)	2.863(1)	O(1)–C(2)	1.242(3)
Cu(2)–O(2W)	1.941(2)	N(1)–C(2)	1.321(3)
O(1A)–C(2A)	1.238(3)	N(1)–C(3)	1.456(3)
N(1A)–C(2A)	1.326(4)	C(1)–C(2)	1.496(3)
N(1A)–C(3A)	1.453(4)	C(3)–C(3)#3	1.531(5)
C(1A)–C(2A)	1.498(4)	O(1E)–C(2E)	1.28(2)
C(3A)–C(3A)#1	1.522(6)	C(1E)–C(2E)	1.38(2)
O(1B)–C(2B)	1.247(3)		
N(1B)–C(2B)	1.323(4)		
N(1B)–C(3B)	1.461(4)		
C(1B)–C(2B)	1.501(4)		
C(3B)–C(3B)#2	1.512(6)		
O(1E)–C(2E)	1.33(2)		
C(1E)–C(2E)	1.40(1)		
Compound 1		Compound 2	
O(1W)Cu(1)Cl(1)	88.75(7)	O(1W)Mn(1)Cl(1)	85.97(1)
O(2W)Cu(2)Cl(2)	89.87(7)	O(2W)Mn(2)Cl(1)	86.01(1)
C(2A)N(1A)C(3A)	124.7(3)	Mn(1)Cl(1)Mn(2)	94.68(3)
O(1A)C(2A)N(1A)	122.3(3)	C(2)N(1)C(3)	122.2(2)
O(1A)C(2A)C(1A)	120.9(3)	O(1)C(2)N(1)	121.6(2)
N(1A)C(2A)C(1A)	116.8(3)	O(1)C(2)C(1)	121.4(2)
N(1A)C(3A)C(3A)#1	111.2(3)	N(1)C(2)C(1)	116.9(2)
C(2B)N(1B)C(3B)	123.8(2)	N(1)C(3)C(3)#3	110.4(2)
O(1B)C(2B)N(1B)	122.3(2)	O(1E)C(2E)C(1E)	137.0(18)
O(1B)C(2B)C(1B)	121.1(3)		
N(1B)C(2B)C(1B)	116.7(2)		
N(1B)C(3B)C(3B)#2	110.7(3)		
O(1E)C(2E)C(1E)	118.4(19)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+1$ #2 $-x+1, -y+1, -z$ (1)

#3 $-x+2, -y+1, -z+1$ (2)

The interactions between inorganic and organic components of the cocrystals are based on hydrogen bonding formed between the donor groups and acceptor groups, Table 3. Water molecules represent donor groups for carbonyl acceptor groups from EBA resulting in two H bonds (2.784(2) și 2.677(2) Å). $-\text{NH}$ (1) is the donor group which forms one H bond with Cl(1) acceptor group (3.285(2) Å).

EBA molecule is centrosymmetric composed of two plane fragments sharing C(3)–C(3)* bond, *trans* related to C–C central bond. The torsion angle N(1)C(3)C(3)*N(1)* is 180°. This angle has the same value in EBA molecule,²⁰ while in coordination compound of Co with EBA¹⁵ the angle is 61° due to conformation changes determined by coordination of EBA.

Table 3

Hydrogen bonds for **2** (Å and deg.)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformations for A
O(1W)–H(1)···O(1)	0.78	2.01	2.784(2)	174	x, y, z
O(2W)–H(1)···O(1)	0.80	1.89	2.677(2)	168	$-x+3/2, y, -z+2$
N(1)–H(1)···Cl(1)	0.86	2.45	3.285(2)	163	$-x+2, y-1/2, z$

Structure of **1** resembles to **2**. Replacing Mn(II) with Cu(II) leads to different geometrical parameters of the coordination polyhedron but the symmetry is C_i . The coordination polyhedron of Cu (II) is an extended octahedron 4+2 type. The interatomic distances for Cu(1) are Cu(1)–Cl(1) 2.297(1), Cu(1)–O(1W) 1.981(2), Cu(1)–Cl(2) 2.845(1) Å and for Cu(2), Cu(2)–Cl(2) 2.298(1), Cu(2)–Cl(1) 2.863(1) and Cu(2)–O(2W) 1.941(2) Å, Table 2.

A similar structure to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has been described by Wells²¹ with length values 2.28, 1.93 and 2.91 Å. It is important to be mentioned that *trans* configuration was established for copper atoms as well as for the manganese atoms. The per-

spective of the crystal along a axis shows the inorganic chains $\{\text{CuCl}_2(\text{H}_2\text{O})_2\}_n$ (**1**) interacting with EBA molecules, fig.4,a.

A survey of Cambridge Crystallographic Data¹⁸ has shown the existence of a similar inorganic chain,²² $\{\text{CuCl}_2(\text{H}_2\text{O})_2\}_n$ as a part of the compound trimethylammonium diaqua-dichloro-copper chloride.^{19,22}

The interactions between the polymer chains and EBA molecules in cocrystal **2** are similar to ones discussed for **1**. The parameters of the hydrogen bonds (lengths, Å and angles) are presented in Table 4.

Table 4

Hydrogen bonds for **1** (Å and deg.)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformations for A
O(1W)–H(1)···O(1B)	0.88	1.88	2.739(3)	164	$-x, -y+1, -z$
O(1W)–H(2)···O(1A)	0.91	1.83	2.734(3)	170	$x, y, z-1$
O(2W)–H(1)···O(1A)	0.78	1.94	2.692(3)	162	$x, y, z-1$
O(2W)–H(2)···O(1B)	0.96	1.77	2.706(3)	164	$x+1, -y+1, -z$
N(1A)–H(1)···Cl(1)	0.86	2.39	3.223(3)	164	x, y, z
N(1B)–H(1)···Cl(1)	0.86	2.46	3.287(3)	161	x, y, z
O(1E)–H(1)···Cl(2)	0.82	2.71	3.441(9)	150	x, y, z

In the unit cell the inorganic part is surrounded by two centrosymmetric independent EBA molecules described with the same parameters as in the case of **1**.

In both compounds, **1** and **2**, the solvent molecules establish weakly interactions in the crystals and occupy partially the empty channels from the

tridimensional networks (Fig. 4.a, b). Upon removal solvent molecules the total potential accessible free volume corresponds to approximately 15.3% (**1**) and 15.7% (**2**) of the unit cell volume.

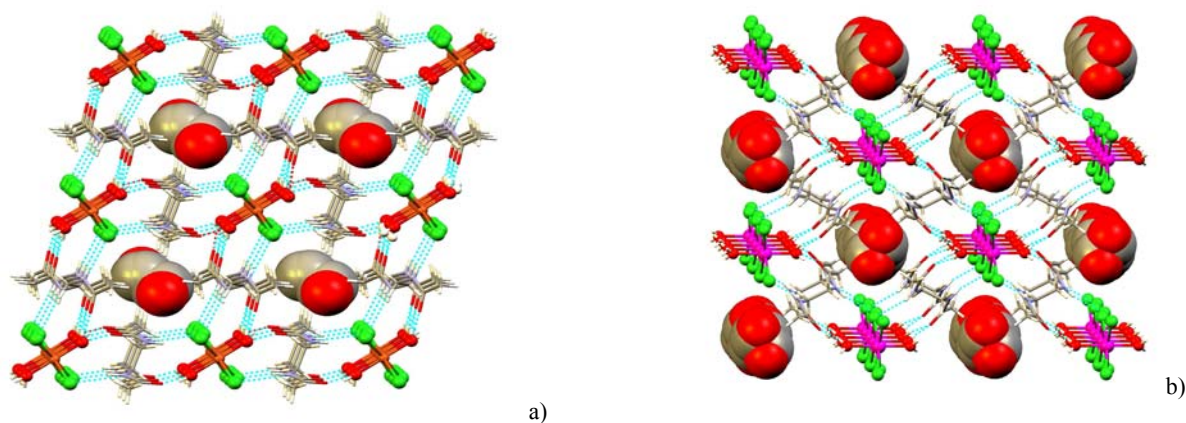


Fig. 4 – a. View of the crystal structure of $\text{CuCl}_2(\text{H}_2\text{O})_2 \cdot \text{EBA} \cdot 0.5 \text{C}_2\text{H}_5\text{OH}$ along a axis.
b. View of the crystal structure of $\text{MnCl}_2(\text{H}_2\text{O})_2 \cdot \text{EBA} \cdot 0.5 \text{C}_2\text{H}_5\text{OH}$ along c axis.

IR spectra

The overlapped spectra of the compound EBA, (1) and (2) are presented in Fig. 5.

There are only little differences between FTIR spectrum of ethylene bis(acetamide) (EBA) and those of the compounds (1) and (2) due to the existence of hydrogen bonding. The stretching vibra-

tion corresponding to C=O bond is shifted from 1635 cm^{-1} (EBA) to 1606 cm^{-1} (1) and 1613 cm^{-1} (2) respectively. The band corresponding to the bending vibration of N-H bond is displaced from 1549 cm^{-1} (EBA) to 1568 cm^{-1} (1), 1561 cm^{-1} and the band assigned to $\nu_{\text{N-H}}$ is shifted from 3285 cm^{-1} (EBA) to 3262 cm^{-1} (1), 3279 cm^{-1} (2).

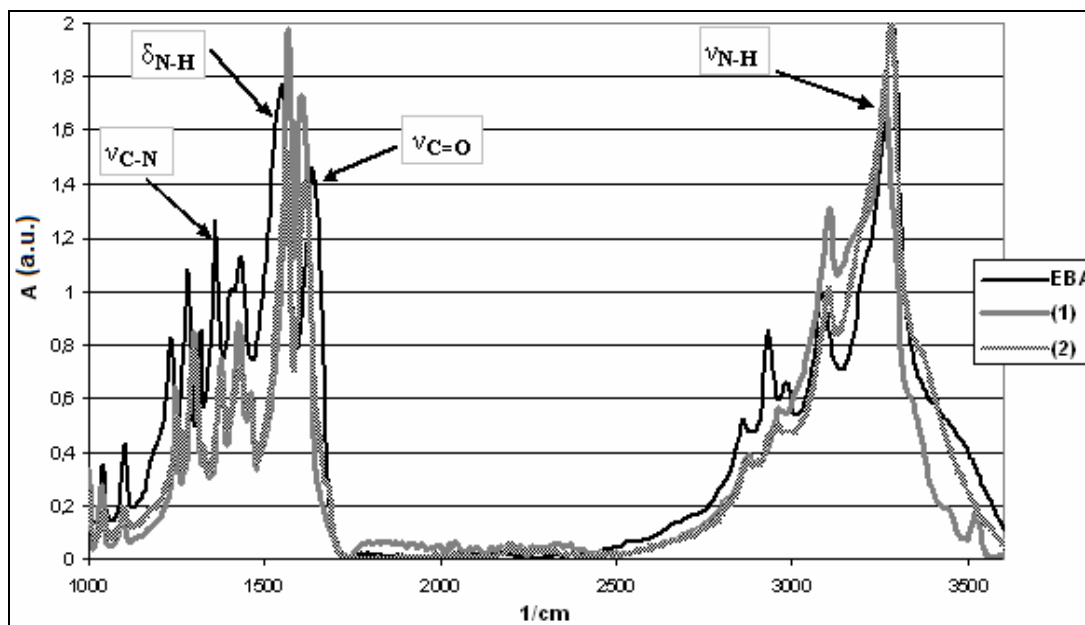


Fig. 5 – FTIR spectra for EBA, (1), (2).

UV-VIS reflectance spectra

The electronic spectrum of (1) contains a large band at 750 nm assigned to ${}^2E_g \leftarrow {}^2T_{2g}$ which confirms the octahedral geometry of Cu (II). The UV-

VIS spectrum of (2) contains bands of very low intensity assigned to the spin-forbidden transitions ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ specific to Mn(II) in octahedral distorted geometry (Fig. 6).

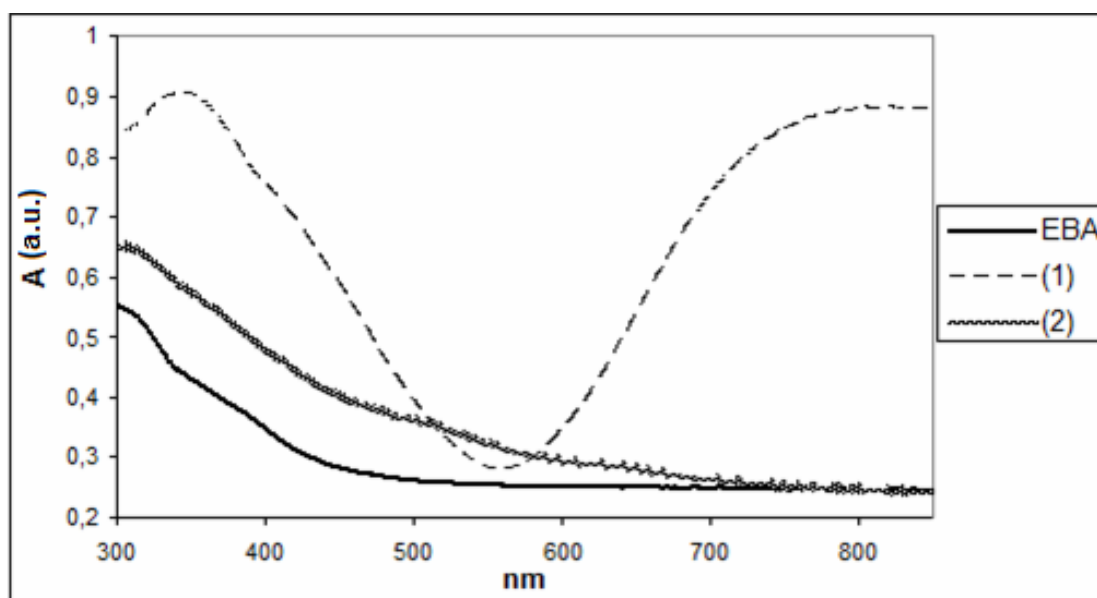


Fig. 6 – UV-VIS spectra of EBA, (1), (2).

EXPERIMENTAL

All reagents were used as purchased.

EBA synthesis:

N, N'-ethylene bisacetamide was synthesized from ethylenediamine and acetic acid distilled at 15 mmHg, 3 h. The obtained solid was recrystallized from isopropyl alcohol. Anal. Found (%) C, 50,78; H, 8,78, N, 19,65. Calculated for C₆H₁₂N₂O₂ (%) C, 50,00; H, 8,33; N, 19,44.

IR (cm⁻¹): 3285 vs, 1635 s, 1549 vs, 719 m.

¹H-RMN (DMSO-d₆, δ_{ppm}, J (Hz)): 1.77 (s, 6H, CH₃); 3.04 (t, 2.5, 4H, CH₂); 7.87 (s, 2H, NH).

¹³C-RMN (DMSO-d₆, δ_{ppm}): 169.53 (C=O), 38.48 (CH₂), 22.70 (CH₃).

UV-VIS (λ_{max}, nm): 236.

Synthesis of inorganic-organic species

(MnCl₂(H₂O)₂), 2(C₃H₆NO), 0.5(C₂H₆O)

A solution of N, N'-ethylene bisacetamide dissolved in ethanol is mixed with a solution of MnCl₂·4H₂O in water, 2:1 molar ratio. The solution is left to crystallize and after a week transparent crystals were obtained.

Calculated for MnC₇H₁₉N₂O₄.5Cl₂: C= 25,53%; H= 5,77%; N= 8,51%;

Experimental: C= 25,23%; H= 5,65%; N= 8,76%.

Electrical molar conductivity, Λ = 22 μS/cm, non-electrolyte

(CuCl₂(H₂O)₂), 2(C₃H₆NO), 0.5(C₂H₆O)

A solution of N, N'-ethylene bisacetamide dissolved in ethanol is mixed with a solution of CuCl₂·2H₂O in water (2:1 molar proportion). The solution is left to crystallize and after three days green crystals were obtained.

Calculated for CuC₇H₁₉N₂O₄.5Cl₂: C= 24,87%; H= 5,62%; N= 8,29%;

Experimental: C= 24,89%; H= 5,48%; N= 8,90%.

Electrical molar conductivity, Λ = 15 μS/cm, non-electrolyte

Chemical elemental analyses were carried out on a Carlo Erba M1106 Elemental Analyzer. UV-VIS spectra were obtained using a Jasco V-560 spectrophotometer and FTIR spectra were recorded on a Bruker spectrometer in the range of 4000-400 cm⁻¹.

¹H-RMN and ¹³C-RMN were performed on a Varian 300 MHz spectrometer in DMSO-d₆.

Electrical molar conductivities were measured in N,N-dimethylformamide (10⁻³ M solution) on OK-114 RADELKIS Conductometer at 25°C

X-ray diffraction measurements were performed on a BRUKER diffractometer with graphite monochromated Mo K_α radiation using ω rotations. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97)²³ by fullmatrix least-square procedures on F2. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Centre, CCDC 727827 & 727828

CONCLUSIONS

Cocrystal inorganic/organic structures of MX₂·2H₂O/organic molecule type (M-first row transition metal) were described for the first time. The geometry of the coordination polyhedron is determined by the metal nature and the ligand environment (Jahn Teller effect). Typically for Mn

(II) atoms is compressed octahedral geometry and for Cu (II) atoms, extended octahedral geometry. Cocrystals are stabilized through hydrogen bonds which result in supramolecular assemblies.

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