Asian Journal of Research in Chemistry and Pharmaceutical Sciences

MAGNETIC PROPERTIES IN BINUCLEAR COPPER (II) AND COBALT (II) COMPOUNDS WITH SULFONIC ACID AND DICYANDIAMIDE AS VERSATILE LIGAND

Yenny Avila-Torres[*1], Stephanie Cortes[1], Pablo Marulanda[1], Edwin Florez-Lopez[2]

[1]*Escuela de Quimica, Facultad de Tecnologias, Universidad Tecnologica de Pereira, Pereira, Colombia.
[2]Programa de Quimica, Facultad de Ciencias Básicas, Universidad Santiago de Cali, Pampalinda, Cali, Colombia.

ABSTRACT
The ligands 1-Amino-2-naphthol-4-sulfonic acid (AANS) and dicyandiamide (DCD) stabilized two binuclear compounds with copper (II) and cobalt (II). AANS suggested bidentate coordination towards metal center in accordance with spectroscopic evidences in both compounds. The acetate group serves as bridge ligand which allowing antiferromagetic and ferromagnetic coupling for cobalt (II) and copper (II). The sulfonic acid presented an unusual behavior. In presence of acetate salt this group did not acts such as Bronsted Lowrry acid neither Lewis base. The coordination was towards amine and alcohol group. This may be due to space availability around metal center in square pyramidal and octahedral geometry.

KEYWORDS
Binuclear, Coordination, Deprotonation, Copper (II) and Absorption.

Author for Correspondence:

Yenny Patricia Avila Torres,

Escuela de Química, Facultad de Tecnologías,

Universidad Tecnológica de Pereira, Pereira,

Colombia.

Email: yennypatricia.avila@utp.edu.co

INTRODUCTON
Sulfonate groups have showed coordination modes different with relationship to metal ion. One-dimensional chains with silver ions have been stabilized and the sulfonic group constituted a bridge between metal ions. Luminescent properties were associated with these kind polymeric structures[1-4]. The presence of sulfonic acid group can be successfully incorporated in porous coordination polymer. The topology involved give to place adsorption for carbon dioxide in UiO-66 structure type. This easiness let mixed ligand in guest structures[5-6]. Also has been founded that sulfonic acid when is exposed on the pore

surface can be act as strong Bronsted acid. This behavior give to place catalytically hydrolyzes cellulose into mono and disaccharides with durability properties in catalytic reaction[7].

For Cu(II), Ni(II), Zn(II), Mg(II), Ba(II), Sr(II) and Cd(II) chemical analyses and physic-chemical evidence has been showed coordination to disodium salt when the ligand is tridentate. For example, 2-nitroso-1-naphtol site is involved in metal chelation, where the hydroxyl group is functional at either site[8]. With camphor group inside sulfonic acid was possible to study new chiral complexes with Lanthanides (III), in where the metal ions favors delocalization electronic and charge transfer such consequence of chelate effect[9].

On the other hand, the guanidine groups can be considerate as N-based donor ligands in coordination chemistry. These compounds have shown varied coordination modes at metals from across the periodic table[10-14]. The same manner that sulfonate group, the coordination in guanidine is associated to high basicity. The electron pair is involved in π interaction $[(NMe_2)_3]^+$ and the ligand present a tridentate behavior. If an imine is stabilized give to place to adduct through of monodentate coordination. There is competition between carbonyl charge and imine charge.

In biological process, this ion participates in recognition of anionic substrates, binds cofactors, forms internal hydrogen bonds and salt bridges and enhances protein hydrophilicity. Additionally to mentioned previous reactivity an environment hydrophobic and macro dipole of the proximate guanidine group diminish its basicity[14].

The most thoroughly investigated binuclear compounds by far are those involving copper (II) ions, where the interaction occurs between two local doublet states. There is a diamagnetic ligand capable of transmitting the electronic effects between metal centers. About 95% of copper (II) binuclear compounds present an antiferromagnetic interaction. Bleaney and Bowers[15,16] interpreted the magnetic interaction phenomenon within of copper (II) acetate monohydrate. The EPR spectra resemble those of triple states rather than doublet states expected non-

interacting copper (II) ions. The metal centers are in square pyramidal environments, with oxygen atoms from acetate groups in the basal planes and water molecules occupying the apical positions. The Cu….Cu separation is equal to 2.64 Å. The χ vs. T plot presented a broad maximum around 265 K and becomes almost negligible below 100 K. This effect, which is often observed for polymetallic compounds with a single ground state, is not intrinsic to the compound but is due to the presence of a very small amount of non-coupled species in the sample. The guanidine group is a versatile ligand such as azido bridges[17]. The copper (II) binuclear compounds present magnetic properties with rather intriguing versatile. The planar network in cryptate structures have shown antiferromagnetic strongly coupled. Even at room temperature the triplet excited state is totally depopulated. All the copper (II) binuclear compounds with symmetrical end- to- end azido bridges present such a strong antiferromagnetic interactions[18]. The azido groups bridge in an end- to- end fashion between the apical positions of one copper atom and the basal plane of the adjacent copper atom have shown ferromagnetic interactions. On the other hand, cobalt (II) polynuclear compounds have shown long range magnetic ordering on the basis of dipolar interactions between layers, large coercive fields produced by the alignment of magnetic moments, in addition to the synergy between crystalline arrangement and single ion anisotropies. Cobalt (II) trinuclear compounds have shown super- paramagnetic- like properties, exhibiting both a frequency dependent out- of- phase ac magnetic susceptibility and hysteresis in a plot of magnetization vs. applied dc magnetic field, therefore they could be considered as a SMM[19].

In this paper, we present the synthesis coordination compounds from deprotonated and protonated ligands (Figure No.1), 1-Amino-2-naphthol-4-sulfonic acid (AANS) and dicyandiamide groups (DCD) with copper (II) and cobalt (II) ions. The $[Cu_2 (AANS)_2 (DCD) (CH_3COO)_2 EtOH]$ (1) and $[Co_2(AANS)_2 (CH_3COOH)_2 (NSC)_2 (DCD)_2]$ (2) suggested dimeric complex using spectroscopic techniques such as: mass spectrometry, infrared, UV- Vis spectroscopy, variable

magnetization, elemental analysis, XPS and atomic absorption.

Experimental

Physical measurements

FT IR spectra were recorded with a (Perkin-Elmer 1600) spectrophotometer using KBr pellets (4000-400 cm^{-1}). The UV-Vis spectra (transmittance, over the range 200-800 nm) were recorded on a Spectronic 3600 Shimadzu spectrophotometer. Elemental analyses were performed on a Fisons EA 1108 elemental analyser. The chemical analysis was obtained using X-ray photoelectron spectroscopy (XPS). This was performed using a VG Microtech ESCA2000 Multilab UHV system, with an Al K_α x-ray source (hv = 1486.6 eV) and a CLAM4 MCD analyzer. XPS spectrum was obtained at 55° from the normal surface in the constant pass analyzer energy mode (CAE), $E_0 = 50$ and 20 eV for survey and high resolution narrow scan. Peak positions were referenced to the background silver $3d_{5/2}$ core level at 368.20 eV, having a FWHM of 1.00 eV, Au $4f_{7/2}$ in 84.00 eV and C 1s hydrocarbon groups in 285.00 eV central peak position. The XPS spectra were fitted with the program SDP v 4.1[20]. The XPS error is based considering a detection limit estimated to be 0.1% in mass and uncertain propagation. For deconvolution analysis the uncertain was estimated at 5% (ie ±0.05 eV).

For magnetic measurements was used Kepcocurrent sourceATE75-15M, Electromagnet Phylatex, Hall sensor CASSY Lab Leybold, acquisition card NI PCI-6221 DAQ (DAQ) from National Instruments and Magnetic susceptibility measurements were carried out with a pendulum-type magnetometer (MANICS DSM8) equipped with an Oxford CF 1200 S helium continuous-flow cryostat working in the temperature range 300 - 4 K in a magnetic field of 3 Oe.

MATERIAL

The metal salt $Cu(OAc)_2·4H_2O$ and $Co(SCN)_2$, methanol and ligands (J.T. Baker) were used without further purification. The acetonitrile, methanol and ethanol solvents were acquired in J.T. Baker.

Synthesis of coordination compounds

Synthesis of [Cu₂(AANS)₂ (DCD) (CH₃COO)₂ EtOH] 2H₂O(1)

To a solution of DCD (1 mmol) in methanol (15 mL), $Cu(CH_3COO)_2$ $4H_2O$ (1 mmol) was added. The mixture was stirred for 15 minutes and refluxed by 2 hours in neutral medium. A green precipitate appeared immediately purified with methanol. Yield 82%. Anal. Calcd. for $Cu_2C_{26} H_{24} N_6O_{13}S_2$: C%, 38.4; H%, 2.8; N%, 10.7; S%, 7.9; Exp: C%, 38.2; H%, 2.8; N%, 10.5; S%, 7.6.IR (KBrv/cm^{-1}): 1040(v_{as} CO), 3500 (v_{as} NH₂), 3420(v_s NH₂), 1578 (v_{as} SOO), 1525 (v_{as} SOO), 1254(v_{as} S-).[19] MS (EI) m/z (%):64 (96), 130 (98), 159 (90), 218 (12), 254 (27), 283 (12), 436 (52).

Synthesis of [Co₂(AANS)₂ (CH₃COOH)₂ (NSC)₂ (DCD)₂] (2)
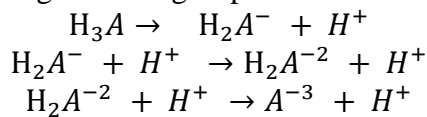
To a solution of DCD (1 mmol) in methanol (15 mL), $Co(SCN)_2$ (1 mmol) was added. The mixture was stirred for 15 minutes and refluxed by 2 hours. A red precipitate appeared immediately purified with methanol. Yield 74% Anal. Calcd. for $Co_2C_{20}H_{20}N_6O_{13}S_2$: C%, 32.7; H%, 2.8; N%, 11.4; S%, 8.7; Exp.: C%, 33.8; H%, 2.9; N%, 11.9; S%, 9.1. IR (KBrv/cm^{-1}): 1030(v_{as} CO), 3480 (v_{as} NH₂), 3420(v_s NH₂), 1578 (v_{as} SOO), 1525 (v_{as} SOO), 1254 (v_{as} S-), 2250 ($v(N_2$-C-N)$_{st}$), ~2180 (v C=N), ~1582 (v NH₂), ~1225(v_{st} C-NH₂).[19] MS (EI) m/z (%):57 (62), 69 (98), 130 (30), 159 (27), 216 (12).

RESULTS AND DISCUSSION

Characterization for conjugate base of AANS ligand

The ligand was deprotonated using sodium hydroxy in solution 0.01 M. The inflection points describe hydrogen losses in basic medium, (Figure No.2). The AANS donates three protons in acid-base reactions, three dissociation stages corresponding to the sulfonic acid, alcohol and the amine group. K_1 (sulfonic acid group desprotonate) must be greater than K_2 (alcohol group desprotonate), and K_3 (amine group desprotonate), which means that each step in the ionization involves a greater extent than previous dissociation. Second proton loss will occur with

greater difficulty than the first, increasing the electrostatic charge for positively charged acid. The sulfonic group is a lewis acid being that in dissolution releases the acidic hydrogen. The spectrum electronic showed shifted to visible spectrum as consequence of resonance in the structure after deprotonation corresponding sulfonic group.

$$H_3A \rightarrow H_2A^- + H^+$$
$$H_2A^- + H^+ \rightarrow H_2A^{-2} + H^+$$
$$H_2A^{-2} + H^+ \rightarrow A^{-3} + H^+$$
$$K_1 = \frac{[H^+][HA^-]}{H_2A}$$
$$pKa = -\log[Ka] = 1.8$$

IR spectrum show ν_{as} and ν_s stretching modes observed at 1580 cm^{-1} and 1520 cm^{-1} and ν_{as}(-S) ~1260 ~1050 corresponding sulfonate group. For primary amine is found ν(N-H)~3400-3100 and ν(C-OH) ~1050 corresponding alcohol group. The UV-Vis spectrum shows n→ π*, π→ π* transitions ~ 220- 250 nm.

Binuclear copper (II) compounds [Cu₂(AANS)₂ (DCD) (CH₃COO)₂ EtOH] 2H₂O (1)
Characterization of absorption and vibrational.
In the UV-Visspectrum two bandsare observed. The first is the charge transfer ML (220-300 nm) and the second corresponds to the transitiond ←d (14892 cm^{-1}) in the expected region for a copper (II), an unpaired electron involved square pyramidal geometry, Figure No.3.

In these compounds the ligand behaves as bidentate, coordinating the copper (II) atom by oxygen atom from alcohol group and the nitrogen atom. The sulfonic group presents modes different for coordination compounds, as is showed in Scheme No.1, it is clear that in this reaction any kind of coordination is not observed in this binder.

In the IR spectra, the alcohol group ν(C-O) at 1040 cm^{-1} and ammine primary vibrations are shifted to lower frequencies upon coordination in **1;** ν_{as} (NH₂), 3500 cm^{-1} and ν_s (NH₂) at 3420 cm^{-1} in comparison with de free ligand [(ν (N-H)~3400-3100, ν (SOO)$_{as}$ 1580 and ν (SOO)$_s$ 1520, ν_{as} (- S) ~1260 ~1050 and ν(C-OH) 1050 cm^{-1}. The carboxylate group presents corresponding vibrations to bridge coordination between metal ions,

ν_{as} (COO$^-$) 1664 cm^{-1} and ν_{as} (COO$^-$) 1569 cm^{-1}, $\Delta\nu$= 95 cm^{-1}. These assignments are overlap with DCD vibrations at ν (C=N) 1641 cm^{-1}, being that is a versatile ligand with some coordination modes, (Scheme 2).

The elemental analyses suggested a binuclear copper (II) compound which describes as follows: the acetate and DCD group are bridged between metal centers in penta coordinate geometry, the AANS ligand is coordinated through C-OH and amine group. There were not observed shifted in sulfonic group. However, the solvent complements coordination sphere. On the other hand, the fragments m/z corresponding to binuclear system were found in mass spectrometry for DCD- Cu-Acetate group-Cu [m/z 254 (27), C₃H₆Cu₂N₄O₂] and Cu(AANS) [m/z 218 (12), C₁₀H₇CuNO].

Due to the fact that the spectroscopic characterization requires enhance, it was realized the XPS spectrum for copper (II) and cobalt (II) in solid state for compound 1 and compound 2. The Figure No.4 shows the main and the satellite peaks of Cu 2p $_{3/2}$ and Cu 2p$_{1/2}$ of the samples. The broad Cu 2p$_{3/2}$ peak has been deconvoluted into two peaks which are marked as peaks A and B. The peak A and B are related to Cu-O and Cu-N respectively, coordination modes corresponding to ligand AANS and two metallic centers.

The chemical shifts in binding energy are often describe with the electronic redistribution or charge transfer of atoms in chemical compounds. A simplified model to explain the chemical shift is the charge-potential model, which states that the ionization energy of a particular level in an atom depends on the potential generated by the valence band electrons and on the surrounding electrons of the atoms. The position of peak A is 932.2-933.8 eV for Cu-O and 930.2-932.1 eV for Cu-N, which in accordance with electronegative effect. Non-evidence of other copper (II) transitions appear in the spectrum in solid state. It suggests that the copper ions in this compound do not present other oxidation states than the 2+ states[21].

The XPS deconvolution[22] spectrum of the C 1s core level shows the contributions of binding energies of (C-CH) 285.78 eV, (C-S) 286.68 eV, (C-N) 287.81 eV, (C=N) 288.73 eV, and (C-O) 289.90 eV, Figure

No.5a. These assignments were done analysing the core levels of the ligand AANS, DCD and $Cu(CH_3COO)_2$, $2H_2O$. For O 1s core level, contributions corresponding to (O-Cu) 530.52 eV, (O-S) 531.01 eV, (O=C) 532.19 were observed, Figure No.5b.The broad peak at 400.34 eV corresponding binding energy N 1s XPS transition, is in agreement with reported values for organic amines coordinated to metal atoms in solid state.

In the follow figure is shown the structure proposed for the binuclear copper (II) compound in accordance with spectroscopic evidence.

Binuclear copper (II) compounds [Co₂(AANS)₂ (CH₃COO)₂ (NSC)₂ (DCD)₂] (2)
Characterization of absorption and vibrational

In the UV-Vis spectrum four bands are observed. The first is the charge transfer ML (31816 cm⁻¹) and other bands corresponds to the transition d← d (v_3= 16063 cm⁻¹ and v_2= 7948 cm⁻¹) in the expected region for a cobalt (II), three unpaired electron involved octahedral geometry. In these compounds the ligand AANS behaves as bidentate, coordinating the cobalt(II) atom by oxygen atom from of alcohol group and the nitrogen atom from of primary amine, 1030(v_{as} CO), 3480 (v_{as} NH₂), 3420(v_s NH₂), 2250 (v(N₂-C-N)st), ~2180 (v C≡N), ~1582 (v NH₂), ~1225(v_{st} C-NH₂). The sulfonic group was not presented shifted after reaction with metal ion. The acetate molecule acts as bridged between metal cents of cobalt (II) and DCD presented coordinated µ1− monodentade. The thyocyanate group completes the sphere octahedral coordination shown the corresponding vibration at 2150 cm⁻¹ in the IR spectrum. The same manner to compound **1**, the fragments m/z corresponding to binuclear system were found in mass spectrometry for [m/z 57 (27), Co], and [m/z 216 (12), Co(AANS)]. In the follow figure is shown the structure proposed for the binuclear cobalt (II) compound.

The XPS measurements for compound 2 presented similar behavior to compound 1. The deconvolution spectrum of the C 1s core level presents an additional contribution corresponding to C-S at 288.5 eV. This behavior shows structural thyocyanate group. N 1s XPS transition is shifted to major energies due effect in S-C-N, 402 eV. Finally, the effective magnetic moment with Gouy method calculated for compound 2 at room temperature presented a value of μ_{eff} =8.7 MB. This parameter describes in the structure two cobalt (II) ions in configuration d7, S=3/2 in octahedral geometry. The μ_{eff} was calculated with total molecular weight.

Magnetic properties in coordination compounds
Magnetic properties for [Cu₂(AANS)₂ (DCD) (CH₃COO)₂ EtOH] 2H₂O (1) compound

The plots $\chi_M T$ vs. T(K) and $1/\chi_M$ vs. T(K) shows behaviour typical of ferromagnetic coupling with substantial stabilization of the triplet ground state. $\chi_M T$ versus T(K), involve an increase in $\chi_M T$ as temperature is lowered, followed by a rapid drop at temperatures (<22 K). The drop in $\chi_M T$ below 22 K suggests the presence of a weak intermolecular antiferromagnetic interaction. The parameters giving the best fit were obtained using a nonlinear regression analysis, show the next results: g= 2.58, 2J= 20.88 cm⁻¹ in χ_M= (Nβ²γ²/KT)(2exp(J/KT)/(1+3exp(J/KT)), where N (Avogadro number), β (Bohr Magneton), and K (Boltzman constant) have the usual meaning, and χ_M is expressed per mole of copper(II). This behaviour is indicating a very good data fit and moderate ferromagnetic coupling up T>22 K, Figure No.7. The EPR spectrum show typical signals for the axial geometry around copper(II), which is consistent with the proposed structure in where the copper(II) presents pentacoordinate geometry. However, is necessary to collect the spectrum at low temperature, due to little splitting for A (Hyperfine coupling value), in where only are observed two signals of the seven expected for this system (2nI+1; n= number metal ions, I= 3/2, spin nuclear value), **figure 8**.

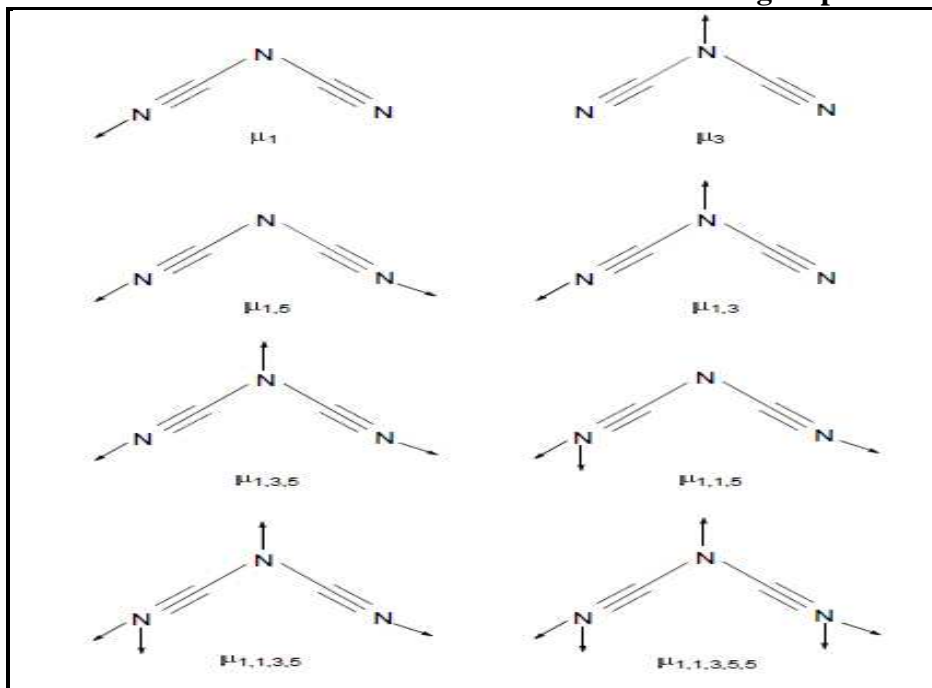## Magnetic properties for compounds [Co₂(AANS)₂ (CH₃COO)₂ (NSC)₂ (DCD)₂] (2)

The splitting of spectroscopic states of d⁷ configuration in high spin, results in two patterns due to the effects: symmetry of the crystal field and spin-orbit coupling. An orbital nondegenerate ground state (⁴A₂) or an orbital degenerate ground state (⁴T₁) in which the orbital levels are separated by spin- orbit coupling. In this case of an orbital nondegenerate gound state, as may be found in tetra- and penta coordinate sites, the

orbital angular momentum is quenched and combined effects of crystal field symmetry and admixture of excited terms through second- order spin-orbit coupling may lead to a splitting of the two Kramers doublets (m_s= ±1/2, ±3/2) of the $^4A_2$ ground- state term in the absence of an applied magnetic field. On the other hand, with and orbital degenerate ground state, the levels are split by the spin-orbit coupling and in general, the combined effects of spin- orbit coupling and distortion of the crystal field from high symmetry lead to a series Kramers doublets. In this case the $^4T_1$ ground state is split corresponding J values of ½ (m_J =±1/2), 3/2 (m_J=±3/2, ±1/2) and 5/2(m=±5/2, ±3/2, ±1/2)[23]. The spectra EPR at 110 K, Figure No.9 is shown that the cobalt (II) is distorted hexa coordinated environment for cobalt(II) in this system; the coordination to metal centre is different in all directions;g_1= 7.38, g_2=4.67, g_3=2.12; with or bitally degenerate ground state[24-27].

Variable temperature susceptibility data for this compound show at room temperature, $\chi_M T$ value of 9.24 cm^3 mol^{-1} K, which is lower than five uncoupled spin free Co (II) ion with S=3/2 (~12.97 cm^3 mol^{-1} K). It suggest spin orbit coupling. The behaviour of the curve $\chi_M T$ vs T at decrease temperature, suggest antiferromagnetic interactions between cobalt canters. This agree with the fit $1/\chi_M$ curve at Curie- Weiss law, θ= -10.0 K, C= 0.08. However, the Hamiltonian model for this system must include isotropic as well as anisotropic exchange contributions, single ion terms describing the effects of zero- field splitting, spin orbit coupling, etc. This fit is complicated, with the results at the moment, Figure No.10[28-35].
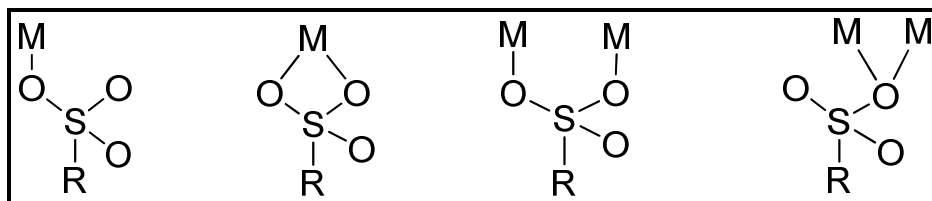
Scheme No.1: Coordination modes for sulfonic group
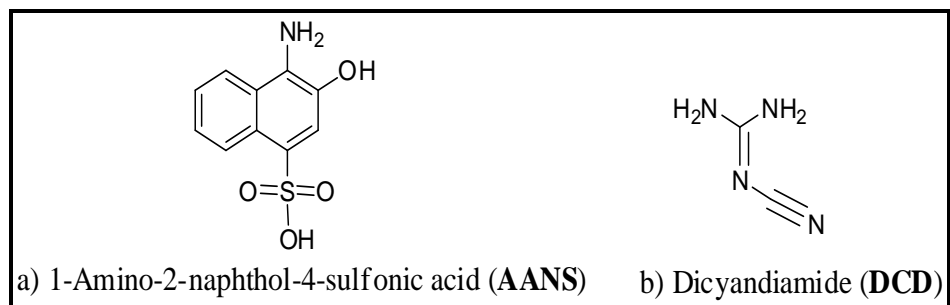

Scheme No.2: Coordination modes for DCD ligand

a) 1-Amino-2-naphthol-4-sulfonic acid (**AANS**)   b) Dicyandiamide (**DCD**)

Figure No.1: a) AANS, b) DCD

a). AANS to pH= 7,2

b). pH= 8.2   pH= 5.2

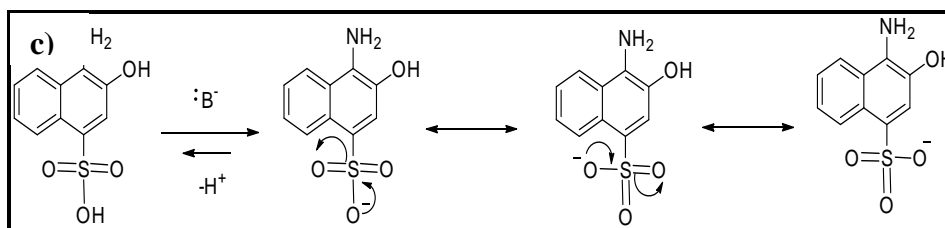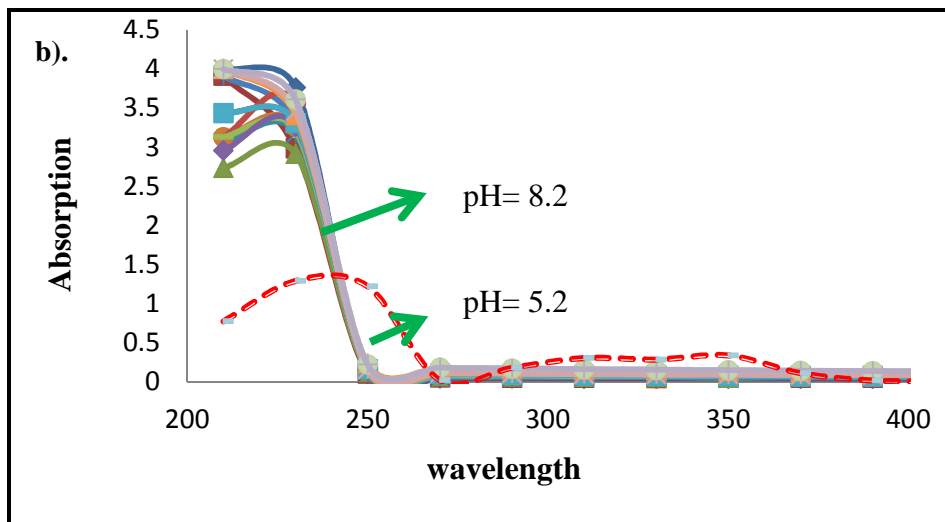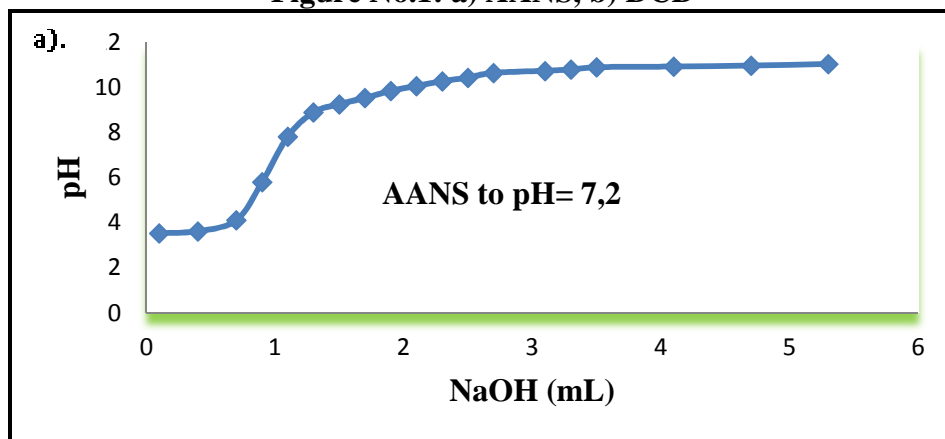c) Resonance structure of conjugate base AANS ligand

Figure No.2: a) Deprotonation curve in AANS, b) Electronic spectrum between 200 nm- 400 nm, c) Resonance structure of conjugate base AANS ligand
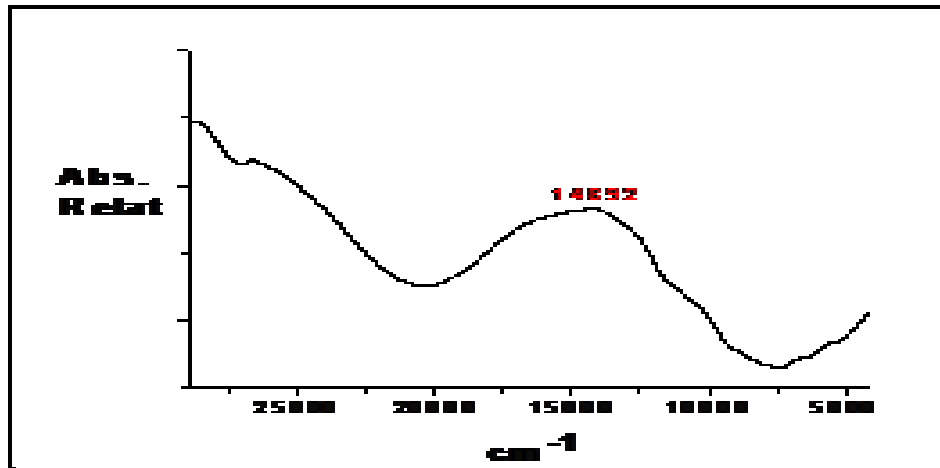
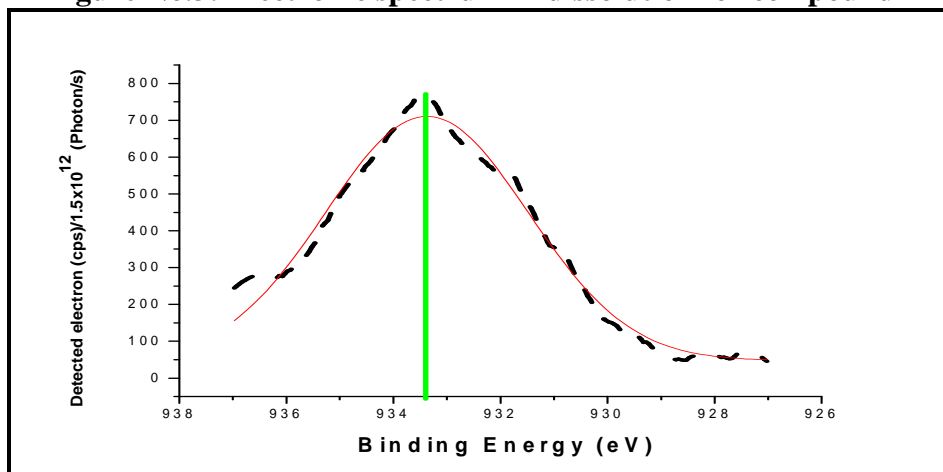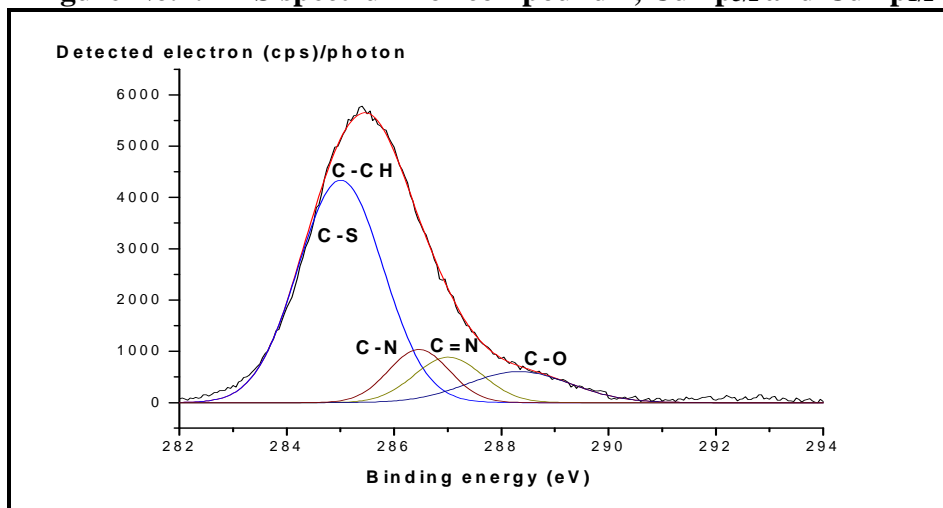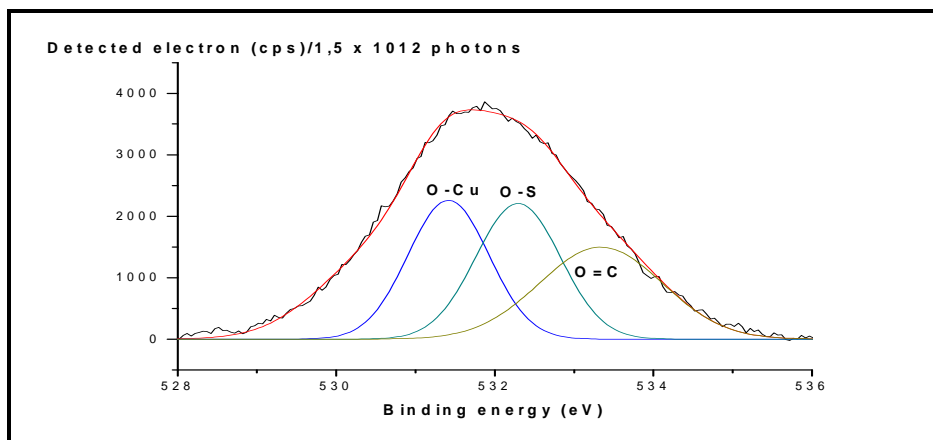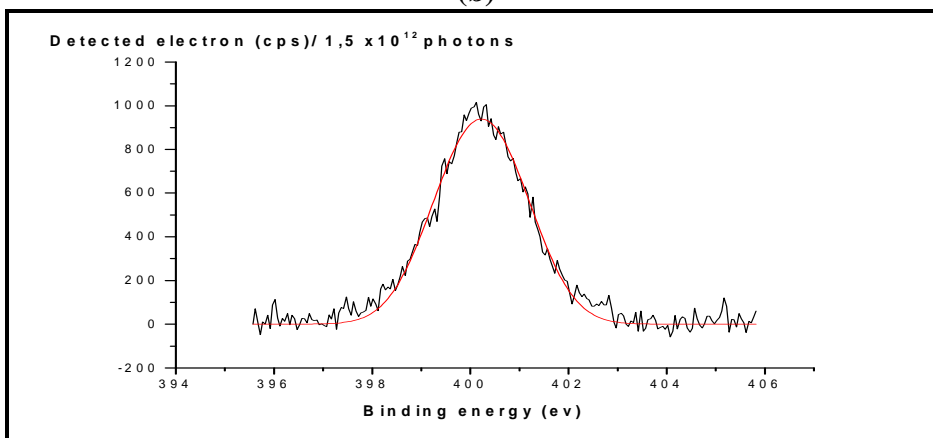**Figure No.3: Electronic spectrum in dissolution for compound 1**

Figure No.4: XPS spectrum for compound 1, Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$

(a)

(b)

(c)

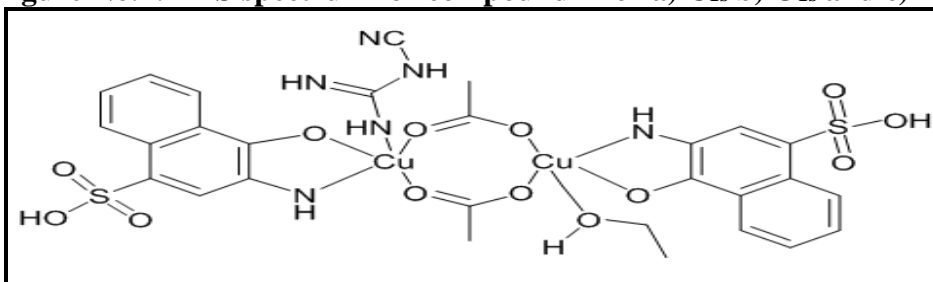**Figure No.4: XPS spectrum for compound 1 for a) C_{1s} b) O_{1s} and c) N_{1s}**

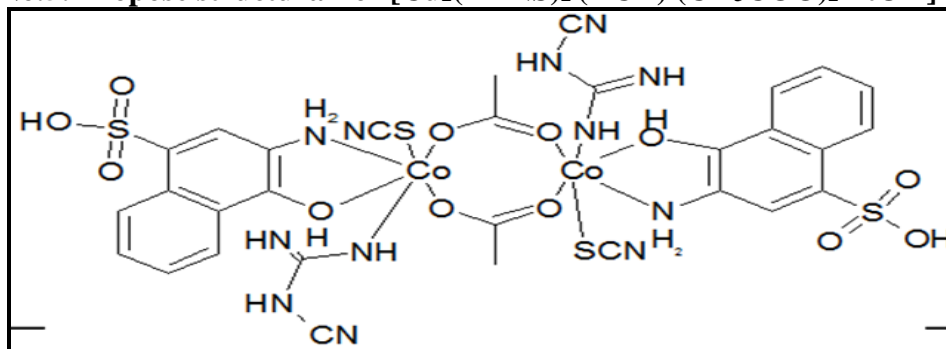**Figure No.5: Propose structural for [Cu$_2$(AANS)$_2$ (DCD) (CH$_3$COO)$_2$ EtOH] 2H$_2$O (1)**

Figure No.6: Propose structural for [Co$_2$(AANS)$_2$ (CH$_3$COO)$_2$ (NSC)$_2$ (DCD)$_2$] (2)
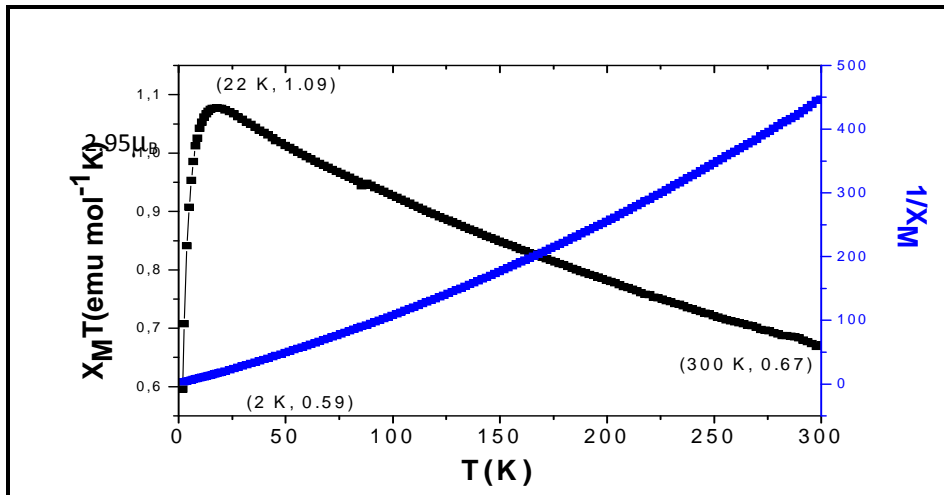
Figure No.7: Susceptibility magnetic at variable temperature for [Cu₂(AANS)₂ (DCD) (CH₃COO)₂ EtOH] 2H₂O (1)
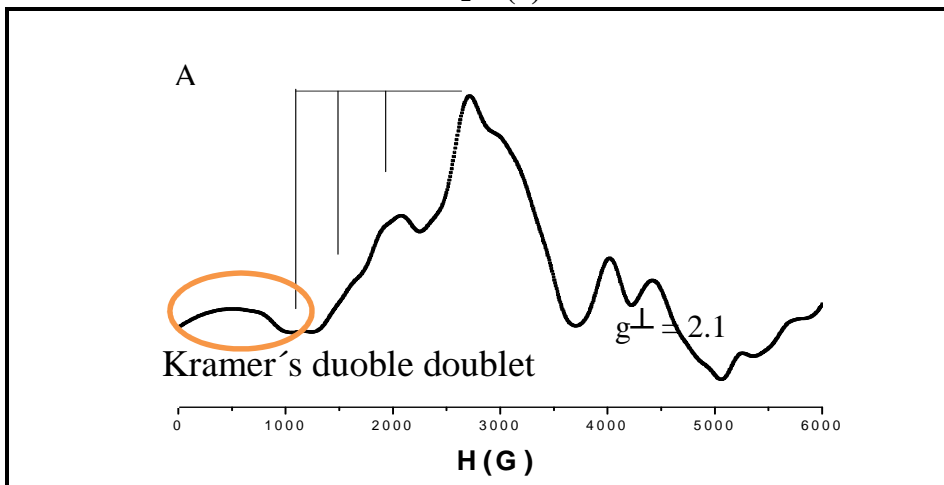
Figure No.8: EPR spectrum at T=110 K for [Cu₂(AANS)₂ (DCD) (CH₃COO)₂ EtOH]·2H₂O (1)
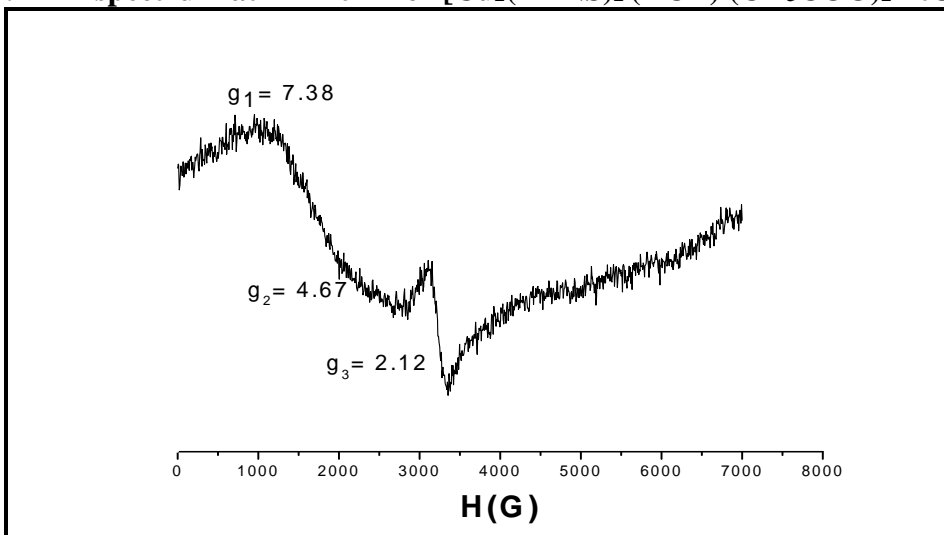
Figure No.9: EPR spectrum at T=110K for [Co₂(AANS)₂ (CH₃COO)₂ (NSC)₂ (DCD)₂] (2)
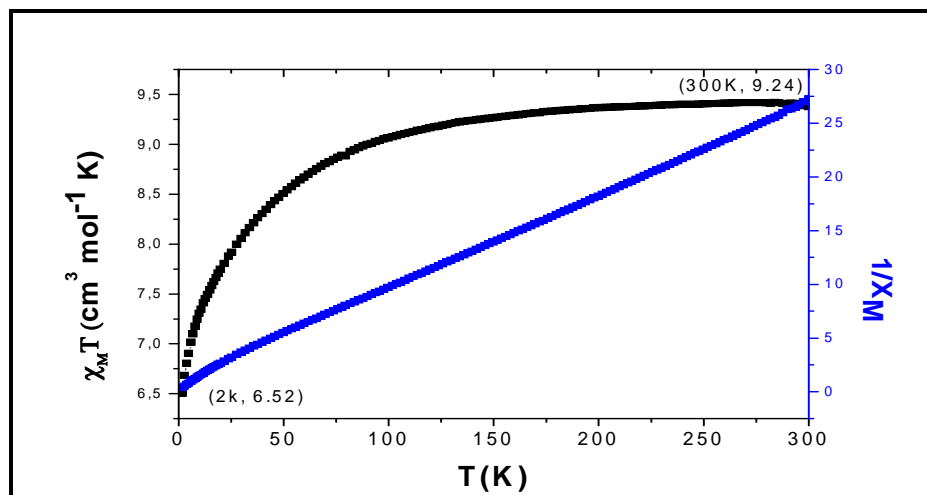
Figure No.10: Susceptibility magnetic at variable temperature for [Co₂(AANS)₂ (CH₃COOH)₂ (NSC)₂ (DCD)₂] (2)

CONCLUSION

The binuclear compounds with copper (II) presents in the structure AANS coordinated in bidentade mode, thorough of amine group and alcohol group. These coordination were suggested by infrared, electronic and XPS spectroscopic on Cu-O, Cu-N in Cu $2p_{3/2}$ and Cu $2p_{1/2}$. The elemental analyses is fixed to proposed structural. On the other hand, the EPR measurement for compound 2 shows a distorted environment in octahedral geometry with the g parameters. The magnetic properties suggested ferromagnetic and antiferromagetic systems for copper (II) and cobalt (II). The magnetic susceptibility is an accordance with molecular weight corresponding to elemental analyses for compound 1 and 2. Finally, this study allowed stablishing to AANS ligand as a versatile coordination in neutral medium. The sulfonic acid presented an unusual behavior. In presence of acetate salt this group did not acts such as Bronsted Lowrry acid neither Lewis base. The coordination was towards amine and alcohol group. This may be due to space availability around metal center in square pyramidal and octahedral geometry.

CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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