

# Synthesis, Single Crystal Structure, and Magnetic Properties of 3-D $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ Complexes

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**Abstract.** A new Cu(II) complexes containing nitroxide radicals  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  has been successfully synthesized. The single crystal X-ray analysis revealed that the compound belongs to monoclinic crystal system (C2/c (#15)). The existence of the  $\text{C}\equiv\text{N}$  radical and water molecules are observed by using infra-red within the range of 4000-500  $\text{cm}^{-1}$  and 3500-3000  $\text{cm}^{-1}$ , respectively. The  $\text{Cu}(\text{NITpPy})_2^{2+}$  units are connected through  $\text{N}(\text{CN})^{2-}$  bridging ligands in 2 coordination developing, respectively, into one-dimensional and two-dimensional polymeric networks. Paramagnetic interactions in the compound appear in the vicinity of room temperature. As the temperature decreased, low dimensional antiferromagnetic interactions established and Cu(II)-radicals antiferromagnetic interactions dominates down to 2 K with  $\mu_{\text{eff}} = 0.8129 \mu_B$

**Keywords :** Magnetism, Polycyanamide Complexes, Nitronyl Nitroxide

## 1. Introduction

There have been challenges to synthesize magnetic complexes compounds by using radical nitronyl nitroxide as ligand [1-5] [1],[2][3],[4][5] . The organic radical nitronyl nitroxide is organic stable at room temperature which possesses single unpaired electron. This unpaired electron could provide the possibility to obtain complexes compounds with unique magnetic properties. The magnetic properties of nitronyl nitroxide consisting complexes can be modified for example by forming bi-radical, or combining nitronyl nitroxide with the other functional groups, using the radical as a ligand to form transition metal organic frameworks [6], [7], [8], [9], [10],[11].

The latest method apparently provides interesting field to study the magnetic interaction between unpaired electrons coming from the nitronyl nitroxide as the ligand and transition metal as the atomic centers. These kinds of complexes having potential application in the field of molecular magnetic. Moreover, the possibilities of combining building blocks of transition metal-radical with a polydentate ligand can provide opportunities to obtain interesting polymeric magnetic complexes [7-11]. Previous work by Dasna *et al.* [7,8,11] shows that obtaining 1D and 2D complexes are possible which is very



important crystallographically as well as to shed light on the search of functional magnetic complexes through structural modification. The reported complexes were consisting of  $2+$  transition metal and nitronyl nitroxide as the building block connected by dicyanamide polydentate ion  $[\text{N}(\text{CN})_2]^-$ .

In this work, we aim to synthesize new building block of complexes  $[\text{Cu}(\text{NITpPy})_2]^{2+}$  bound to  $[\text{Cu}(\text{CN})_3]^{2-}$  ligand. This anion ligand is a polydentate ligand and is designated to provide the possibility of having 3D crystal structure by bridging the building block  $[\text{Cu}(\text{NITpPy})_2]^{2+}$  which would become an impressive system to explore the crystal structure magnetic properties interplay. Apart from that, the unique phenomenon in this synthesis process is the formation of  $[\text{Cu}(\text{CN})_3]^{2-}$  ligand during the crystal growing with slow liquid diffusion H-tube method. This ligand is neither commercially available nor almost impossible to obtain by additional  $\text{CN}^-$  into  $\text{CuCN}$  compound. However, the  $[\text{Cu}(\text{CN})_3]^{2-}$  ligand was formed metathetically during the reaction between tetracyanoethylene (TCNE-) anion and  $[\text{Cu}(\text{NITpPy})_2]^{2+}$ . That is a partial reaction between  $[\text{Cu}(\text{NITpPy})_2](\text{NO}_3)_2$  and  $\text{Li}[\text{TCNQ}]$  in methanol which results in  $[\text{Cu}(\text{CN})_3]^{2-}$  anion. It is suggested that there was possibly occurring reduction-oxidation reaction between  $[\text{TCNE}]^-$  with a certain amount of  $\text{Cu}^{2+}$  from reactant to form the  $[\text{Cu}(\text{CN})_3]^{2-}$  ion. Furthermore, the present of radical ligand in slow liquid diffusion process can accelerate the reduction-oxidation reaction.

The significant results in this contribution concerning the use of unpaired electrons in both nitronyl nitroxide radical and transition metal ions ( $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ) connected by polydentate ligands to design and synthesize functional magnetic complexes compounds. The results have led us to extend the idea that besides using  $[\text{Cu}(\text{CN})_3]^{2-}$  and  $[\text{N}(\text{CN})_2]^-$  ions as ligands, it is also possible applying shorter bidentate ligands such as  $\text{CN}^-$  and  $\text{SCN}^-$  anions. These two latest ligands are expected to shorten the bridging atomic distances to strengthen the magnetic interaction at molecular level. The study of synthesis, structural and magnetic properties of 3D polymeric complexes  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  are described in this article.

## 2. Experimental Method

Compounds of  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  (Aldrich), TCNE (Fluka) were used as purchased. NITpPy was prepared from the procedure described by Ulmanet *et al.* (1970) [12]. The Synthesis was carried out in argon environment and using fresh distilled methanol. The compound  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  obtained by employing slow liquid diffusion in methanolic solvent using H-tube. About 200 mg of  $\text{Cu}(\text{NITpPy})_2(\text{NO}_3)_2$  was placed in one part of H-tube and 100 mg of  $\text{LiTCNE}$  placed in the other part of H-tube. The methanolic solvent was added with a very slowly rate into the tube. Single crystals were obtained after one-month growing process.

### 2.1 Crystallographic Data Collection and Structure Determination

A black brown single crystal was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromated  $\text{Mo-K}\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). The air-sensitive crystals were protected with glue. The cell dimensions and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 centered reflections. The crystal data are given in Table 1. The intensities were collected by  $\theta$ - $2\theta$  scans. There was no significant decay reflected on the three standard reflections measured every hour during data collection and correction. The crystal structures were solved by using SHELXS97 and refined with SHELXL97 [13] by the full-matrix least-square method.

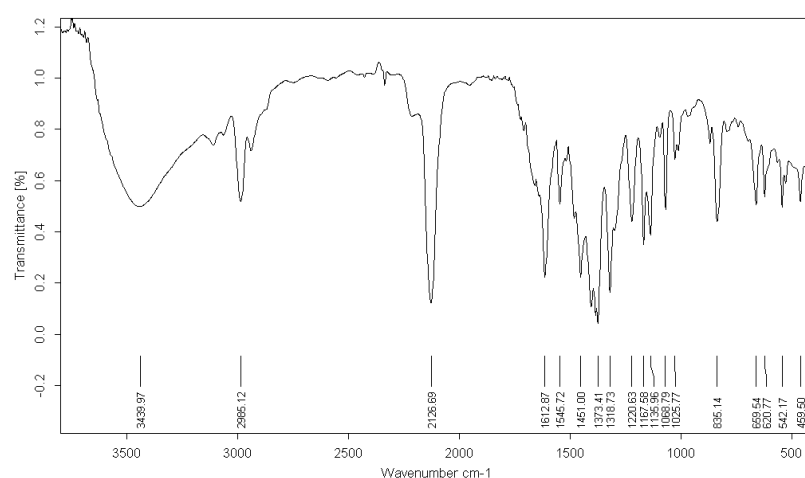
### 2.2 Magnetic and Spectroscopic Measurements

Magnetic measurements have been carried out down to 2 K employing a Quantum Design MPMS-5S SQUID magnetometer. All magnetic investigations were carried out for the polycrystalline sample. The molar susceptibility was corrected for the sample holder and for the diamagnetic contribution of all atoms by using Pascal's table [14]. The FTIR spectra were measured on a KBr pellet sample using IR Bomem-Michelson 100 spectrometer.

### 3. Result And Discussion

#### 3.1 Crystal structure

We have successfully grown enough green crystals with the form of needles to study their structures and magnetic properties. The FTIR study in a KBr matrix within the range of  $4000\text{--}500\text{ cm}^{-1}$  shown in Figure 1 reveals the peaks related to the anion and the  $\text{C}\equiv\text{N}$  radical. The peaks related to the water molecules are also observed between  $3500\text{--}3000\text{ cm}^{-1}$ . Several significant observed peaks are :  $\nu_{\text{C}\equiv\text{N}}$  :  $127(\text{s})$ ;  $\nu_{\text{N-O}}$  :  $1373(\text{s})$ ,  $1136(\text{w})$ ;  $\nu_{\text{N-O}}$  :  $1371(\text{s})$ ,  $1136(\text{w})$ ;  $\nu_{\text{py}}$  :  $1612(\text{m})$ ,  $1546(\text{w})$ ,  $1547(\text{m})$ ,  $1451(\text{m})$ ,  $1404(\text{s})$ ;  $\nu_{\text{O-H}}$  :  $3440(\text{m})$ . The peaks at  $459$  and  $542\text{ cm}^{-1}$  are indicating the presence of Cu-N and Cu-O in the compound.



**Figure 1.** FTIR spectra in KBr pellet of compound  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3]\cdot 2\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$

#### 3.2 Structural Analysis

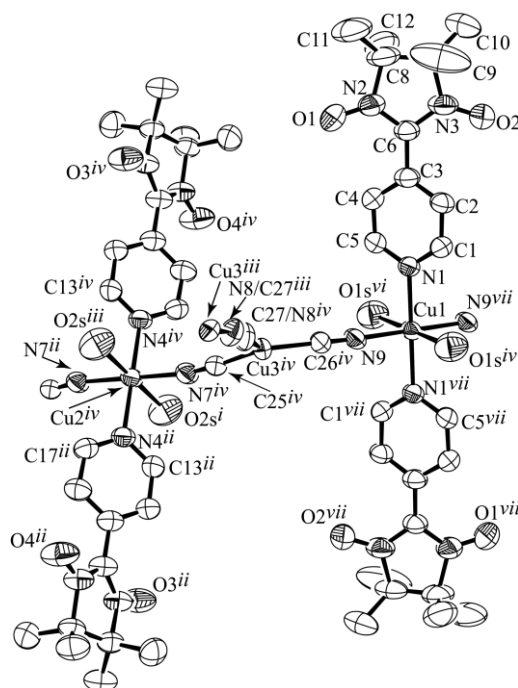
The crystallographic parameters of the  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3]\cdot 2\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$  are summarized in Table 1. The crystal fits the space group C 2/c monoclinic crystal system. Cu1 and Cu2 the atoms are on the inversion centers  $(\frac{1}{4}, \frac{1}{4}, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, 0)$ , the third ion Cu3 is situated in general position.

**Table 1.** Crystallographic data for  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3]\cdot 2\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$

Compound	C57H86Cu4N17O15
Molecular Mass/ $\text{g}\cdot\text{mol}^{-1}$	1503,59
Crystal System	Monoclinic
Space Group	C2/c (#15)
Lattice Parameters:	
a/Å	33,2524(11)
b/Å	13,6270(4)
c/Å	23,5211(6)
$\beta/\text{deg}$	128,247(1)
Volume/Å <sup>3</sup>	8370,3(4)
Z, V Mass (calculated)/ $\text{g}\cdot\text{cm}^{-3}$	4, 1,193
R value	R1 = 0,0706
[I>2 $\sigma$ (I)]	wR2 = 0,2132

The structure ORTEP diagram given in Figure 2 shows that this compound contains two types of copper atoms with different valence state: copper (II) and copper (I). Copper (II) ions (Cu1 and Cu2)

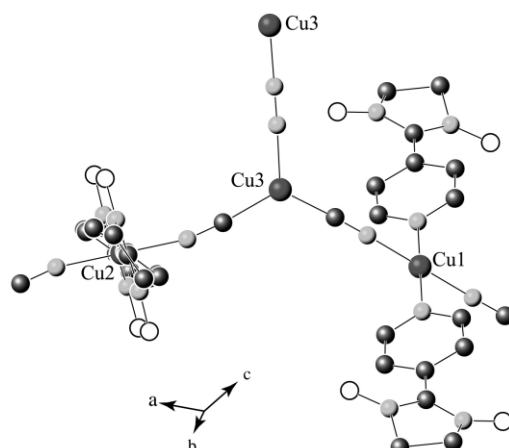
are coordinated in transposition with two radicals through the nitrogen atom of the pyridine ring, two nitrogen atoms of the  $\text{C}\equiv\text{N}$  group, and two atoms of oxygen to methanol. Copper (I) ( $\text{Cu}3$ ) is coordinated by three  $\text{C}\equiv\text{N}$  anions to yield a diamagnetic ligand tridentate  $\text{CuI}(\text{CN})_3^{2-}$  which adopts a distorted trigonal geometry with angles  $\text{C}-\text{Cu}(3)-\text{C}$  ranging from  $114.1(2)^\circ$  to  $124.1(2)^\circ$ .



**Figure 2.** ORTEP view of  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  ( $i = x, 1+y, z-1, ii = 1-x, 1+y, 1/2+z; iii: 1-x, -y, 2-z; iv: x, -y, z-0.5; vii = 1/2-x, -1/2-y, 1-z$ ).

Two nitrogen atoms of the anion  $\text{CuI}((\text{CN})_3)^{2-}$  are each connected to the copper atom of a Cu-group  $(\text{NITpPy})_2(\text{CH}_3\text{OH})_2$ , Cu1 ion on one side and an ion Cu2 the other. In this trans Cu1 or Cu2 ion include another group CuI (CN)  $32^-$ . The angles formed between the anion CuI (CN)  $32^-$  (N8iii plan N7iv, N9) and O1svi plan N9vii, O1siv, N9 on the one hand and the one formed between CuI (CN)  $32^-$  and O2siii, N7iv, O2Si, N7ii are  $67.65(9)$  and  $38.69^\circ(11)$ , respectively. The ion Cu3 is also connected to a third group CN. The position of the nitrogen N8 derives from that of the C27 carbon atom by an axis of symmetry of order two. Thereby the position is statistically half occupied by an atom N8 and a C27 atom. The third nitrogen atom of the anion CuI (CN)  $32^-$  is then linked to an anionic group CuI (CN)  $32^-$ .

The structure of compound 18 is a three-dimensional network whereas Cu ion is bound to a -CN group in a spiral which develops along b axis. The CuII-radical groups adopt a distorted octahedral geometry with average bond lengths Cu-Cu-O and N of  $1.9933(4)$  Å and  $2.4775(49)$  Å, an average angle CuII N-N-90,  $0^\circ$ , and O-Cu-N varying angles of  $81.23(12)$   $98.77^\circ(12)$ . The pyridine group plan and O1, N2, C6, N3, O2 form an angle of  $28.09(41)^\circ$  similar to those observed in the foregoing. The angle of  $75.25(16)^\circ$  formed between the square N1, N9, N1vii, N9vii, Cu1 and Cu plane (CN)  $32^-$  is similar ( $77.84(15)^\circ$ ) that the angle of this anion with the second Cu-radical plan (N4iv, N7iv, N4ii, N7ii, Cuiv). Both Cu-radical groups are in different positions as shown in Figure 3. the O1svi plans N9vii, O1siv, N9 and O2Si, N7iv, O2siii, N7ii an angle of  $82.23(11)^\circ$ . Distances and selected interatomic angles are summarized in Table 2.



**Figure 3.** Position relative group *Cu-radicals* in compound  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ .

**Table 2.** Selected Interatomic Distances (Å) and angles (deg) for  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$

Cu(2)-N(7)	1,951(4)	N(3)-O(2)	1,267(7)
Cu(2)-N(4)	2,036(4)	N(8)iii-C(27)iv	1,162(9)
Cu(1)-N(9)	1,943(4)	N(8)iii-N(8)iv	1,162(9)
Cu(1)-N(1)	2,043(4)	N(7)-C(25)	1,144(6)
Cu(3)-C(26)	1,907(5)	O(1)-N(2)	1,250(7)
Cu(3)-C(25)	1,928(5)	C(1S)-O(1S)	1,417(10)
Cu(3)-N(8)	1,932(5)	C(2S)-O(2S)	1,403(10)
N(6)-O(4)	1,284(6)	O(1S)iv-Cu1	2,4936(48)
O(3)-N(5)	1,269(6)	O(2S)i-Cu2iv	2,4613(50)
N(9)-C(26)iv	1,152(6)		
N(3)-O(2)	1,267(7)	C(25)-Cu(3)-N(8)	114,1(2)
N(8)iii-C(27)iv	1,162(9)	C(1)-N(1)-Cu(1)	121,8(3)
N(8)iii-N(8)iv	1,162(9)	C(5)-N(1)-Cu(1)	120,6(3)
N(7)-C(25)	1,144(6)	C(13)-N(4)-Cu(2)	121,5(4)
O(1)-N(2)	1,250(7)	C(17)-N(4)-Cu(2)	121,4(4)
C(1S)-O(1S)	1,417(10)	C(26)iv-N(9)-Cu(1)	176,8(5)
C(2S)-O(2S)	1,403(10)	C(27)iv-N(8)iii-Cu(3)iii	174,98(16)
O(1S)iv-Cu1	2,4936(48)	C(25)-N(7)-Cu(2)	167,0(5)
O(2S)i-Cu2iv	2,4613(50)	O(1)-N(2)-C(6)	126,3(5)
N(7)-Cu(2)-N(4)I	89,92(17)	O(1)-N(2)-C(8)	121,8(5)
N(7)-Cu(2)-N(4)	90,08(17)	N(7)-C(25)-Cu(3)	174,7(5)
N(9)-Cu(1)-N(1)	89,63(16)	N(9)v-C(26)-Cu(3)	177,9(5)
N(9)-Cu(1)-N(1)ii	90,37(16)	O(1S)iv-Cu(1)-N(1)	98,77(12)
C(26)-Cu(3)-C(25)	124,1(2)	O(1S)vi-Cu1-N(1)vii	81,23(12)
C(26)-Cu(3)-N(8)	121,8(2)	O(2S)iii-Cu(2)iv-N(4)iv	89,99(2)

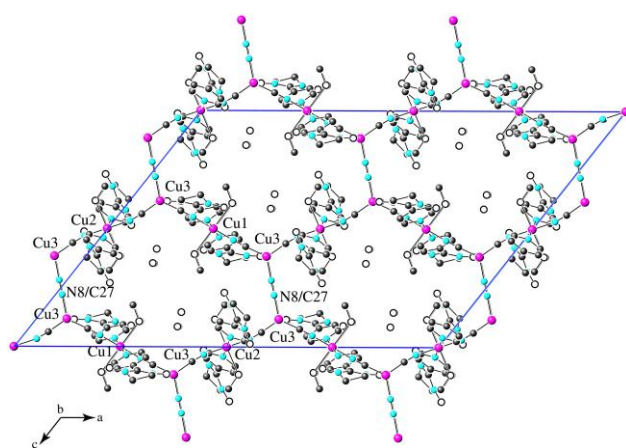
*i* :  $-x+1, -y-1, -z+2$  ; *ii* :  $-x+1/2, -y+1/2, -z+1$  ; *iii* :  $x, -y, z-1/2$  ;

*iv* :  $-x+1, y, -z+5/2$  ; *v* :  $x, -y, z+1/2$

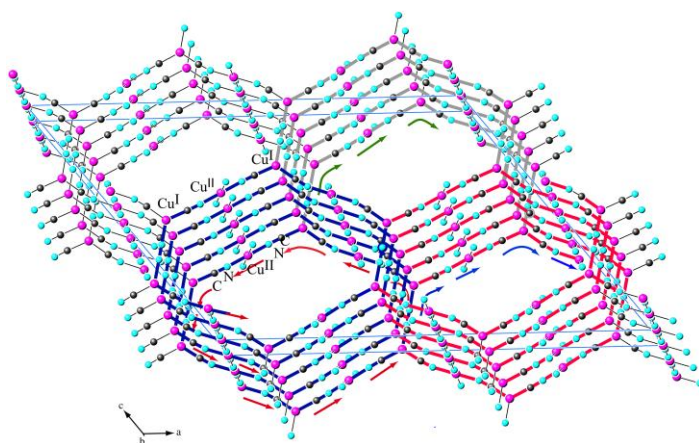
The spiral-like crystal network develops along *b*-direction such that projection on the *ac* plane, a large hexagon is observed (Figure 4) containing four Cu-radical groups. Each hexagon contains ten Copper ions (four six CuII and CuI). The distances between Cu1..Cu3, Cu2 and Cu3 ... Cu3..Cu3 are respectively 4.9980 (6) Å, 4.9719 (5) Å and 5.011 (11) Å.



In a hexagon, the largest diagonal between two copper atoms (Cu 3 ... Cu3) equals 15.213 (1) Å and the distance ... N8 N8 is 17.9681 (5) Å (Figure 4). The water molecules are located inside the spiral in each hexagon without coordinates metal while the methanol molecules are coordinates the CuII atom. In the octahedron CuO2N4, the Cu-O distances are longer than the Cu-N distances indicating the existence of Jahn-Teller distortion for the cation CuII. Figure 5 shows the helical network  $[\text{Cu}_2(\text{CN})_3]_n$ , in which for reasons of clarity, the radicals and solvent molecules are omitted. It shows that the structure consists of an assembly of left or right form spirals. The shortest interactions between groups N-O, 3.727 (11) Å and 3.691 (13) Å, are observed between O3 and O2 ... O3iii O2vii.



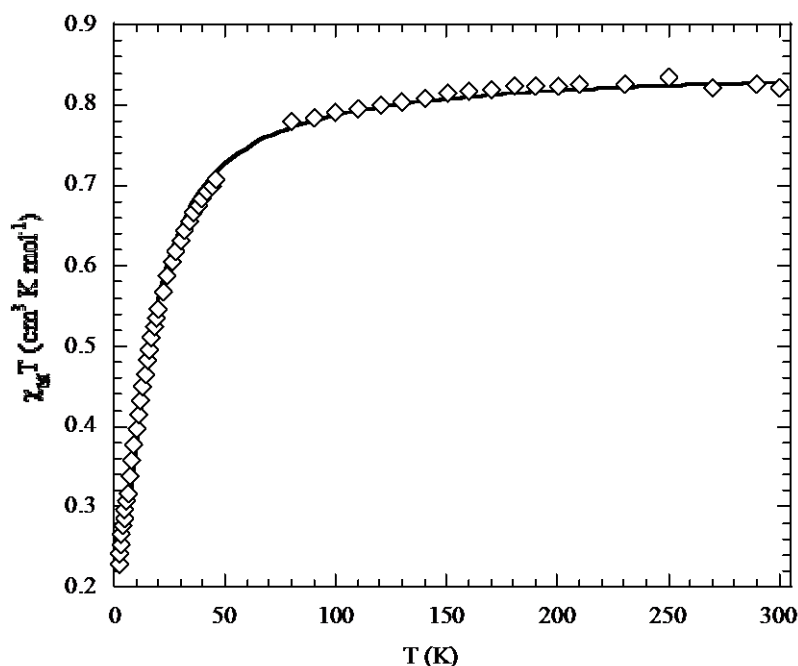
**Figure 4.** Projection on *ac* plan for compound  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ .



**Figure 5.** Network in 3-D for compound  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  whereas radical and solvent are not viewed for crystal structure clarity.

### 3.3 Magnetic Properties

The  $\chi_M T$  data are plotted against  $T$  in the range of 2 K and 300 K shown in Figure 6. At room temperature, the compound exhibits a paramagnetic behavior with a value of  $0.826 \chi_M T \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  which is lower to the expected value coming from the uncoupled spins of Cu(II) ion ( $S = 1/2$ ) and two radicals ( $S = 1/2$ ). When the temperature decreases down to 46 K, the  $\chi_M T$  value decreases gradually and then decreases very fast approaching 2 K indicating the existence of antiferromagnetic interactions between the copper (II) ion and two radicals. This curve is modeled using the same Hamiltonian as for compound 16 pourconduire to an antiferromagnetic coupling constant between Cu-radical,  $J = -13.2$  (3)  $\text{cm}^{-1}$  and a weak intermolecular interaction antiferromagnetic ( $zJ = -0.74$  (20)  $\text{cm}^{-1}$ ) between the magnetic centers, for a value of  $g = 2.0$  and reliability factor  $R = 0.99755$ .



**Figure 6.**  $\chi_M T$  vs.  $T$  for  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$

#### 4. Conclusion

The coordination complexes with formula  $\text{Cu}(\text{NITpPy})_2[\text{Cu}(\text{CN})_3] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  has been successfully synthesized by means of slow liquid diffusion H-tube method in methanolic solution. The complexes obtained shows the 3D crystal behavior with polymeric chain. The building block of  $[\text{Cu}(\text{NITpPy})_2]^{2+}$  is connected by  $[\text{Cu}(\text{CN})_3]^{2-}$  anion ligand results in 3D chain network. The unpaired electrons contributed by  $\text{Cu}^{2+}$  and radicals bound to  $\text{Cu}^{2+}$  ion giving rise antiferromagnetic interaction. The results pave the way to design and synthesis controllable magnetic properties in coordination complexes by using different transition metal ions.

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