

# Synthesis, Spectroscopy and Magnetism of Alkoxo–Bridged Dinuclear Copper(II) Complexes with 2 – Amino – Picolines as the Ligands

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**ABSTRACT:** *The synthesis, spectroscopic and magnetic characterization of a series of new alkoxo–bridged binuclear copper (II) compounds are described. All complexes have the general formula  $[Cu(\mu-OR)(L)_2]_2(ClO_4)_2 \cdot x H_2O$ , in which  $\mu-OR = CH_3O^-, C_2H_5O^-$  or  $C_3H_7O^-$ ,  $L = 2\text{-amino-4-methylpyridine}$  (abbreviated A4PIC) and  $2\text{-amino-5-methylpyridine}$  (abbreviated A5PIC). The title compounds all consist of dinuclear units with alkoxo–bridging group. All complexes have been synthesized in one-step reaction, and characterized by elemental analysis, FTIR and electronic spectra and by magnetic properties. The compounds exhibit strong antiferromagnetic interaction at room temperature. The UV–Vis spectra shows three absorption bands, which can be attributed to  $d-d$  transition of copper (II) ion, ligand→metal charge transition and  $\pi \rightarrow \pi^*$  transition of the ligand. The IR spectra indicates  $Cu_2O_2$  ring vibrations in  $500-570\text{ cm}^{-1}$  range. The magnetic properties of the  $[Cu_2(A5PIC)_4](O-CH_3)_2(ClO_4)_2$  complex has been investigated in the  $5-265\text{ K}$  range and a singlet–triplet energy gap ( $-2J$ ) of  $126\text{ cm}^{-1}$  was observed.*

**KEY WORDS:** *Spin - Spin interaction and Binuclear Copper (II) Complexes*

## INTRODUCTION

The structures and magnetic properties of hydroxo–bridged polynuclear transition–metal complexes have been studied extensively during the last three decades[1]. The magnetic behavior of polynuclear complexes can be estimated by such factors as the electronic structure of bridging and end–capping

ligands and of the complexes [2]. The ligand has a great influence on the metal–metal interaction, e.g.,  $Cu_2(HCO_2)_4(pyridine)_2$  has a magnetic moment of 1.1 BM per copper atom at room temperature, whereas  $Cu_2(CH_3CO_2)_4(pyridine)_2$  has a moment of 1.43 BM [3,4]. The same behavior is observed for the bridging group.

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Metal–metal interactions through bromo bridges are much stronger than through chloro bridges [5]. Compounds containing more than one metal atom with unpaired electron can generally be divided into three main groups, depending on the strength of metal–metal interaction. In the case strong interaction, relatively strong metal–metal bonds occur and the molecule displays simple diamagnetic behavior [6]. In non–interacting type, the magnetic properties of the dinuclear or polynuclear complexes are essentially unchanged from the paramagnetic monomer. In the case of weakly interactins, a weak spin–spin interaction between the unpaired electron of two metal ions occur, leading to low–lying excited states of different spin which can be populated at a thermal energy of ca. 1000  $\text{cm}^{-1}$  [7,8]. The resulting magnetic behavior will be antiferromagnetic or ferromagnetic, depending on whether the low spin (spins paired) or high spin (spins parallel) state is in the ground state [9]. The structural and magnetic properties of many dinuclear copper(II) compounds containing  $\text{Cu}_2\text{O}_2$  system have been investigated previously in order to explain the influence of spin–spin interaction through the bridging system [10,11]. It is now generally accepted that the spin coupling in these kind of complexes occurs through the bridging group by a pathway in square planner oxygen–bridged compounds of type  $[\text{Cu}_2(\text{L})_4(\text{OR})_2]^{+2}$ , where L = monodentate ligand. It is found that the isotropic exchange parameter, 2J, is linearly related to the Cu–O–Cu bridging angle,  $\phi$ , and this correlation has been explained in term of molecular–orbital theory [1,12,13]. Dinuclear copper(II) sites play an important role in biological metalloproteins [13]. The best investigated dinuclear copper(II) proteins are hemocyanin [14], tyrosinase [15,16] or catecholase [17]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of copper(II)–copper(II) coupling is still imperfect. We have been interested in the effects of different R group on the bridging oxygen associated with the change in the magnetic properties. The present paper reports one–step synthesis of a series dinuclear copper (II) complexes, with spectral studies, and the magnetic properties exhibited by copper (II) perchlorate hexahydrate, with 2–amino–4– methylpyridine (A4PIC) or 2– amino

–5–methylpyridine (A5PIC) as the ligand.

## EXPERIMENTAL

### Chemicals

All chemicals were of reagent grade quality, purchased from Merck, (Darmstadt, Germany) and used as received without further purification.

### Synthesis

The coordination compounds were prepared according to the following general procedure: 2 mmol of Cu(II) salt and 4 mmol of the ligand were each dissolved in 25 ml of  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  or *n*-  $\text{C}_3\text{H}_7\text{OH}$ . The Cu(II) salt solution was then added slowly to the ligand solution, thereby preventing any precipitation, filtered to remove any solids and after a week the products separated. Yield ca. 70 %.

Elemental analysis for  $[\text{Cu}_2(\text{A4PIC})_4(\text{O}-\text{CH}_3)_2](\text{ClO}_4)_2$ , [**Comp. 1**]; Found: C, 37.8; H, 4.4; N, 14.00; Cu, 15.24. Calc.: C, 38.05; H, 4.67; N, 13.65; Cu, 15.49 %.

$[\text{Cu}_2(\text{A4PIC})_4(\text{O}-\text{C}_2\text{H}_5)_2](\text{ClO}_4)_2$ , [**Comp. 2**]; Found: C, 38.5; H, 4.40; N, 13.2; Cu, 14.56. Calc.: C, 39.63; H, 4.99; N, 13.20; Cu, 14.98 %.

$[\text{Cu}_2(\text{A4PIC})_4(\text{O}-\text{C}_3\text{H}_7)_2](\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ,

[**Comp. 3**]; Found: C, 39.6; H, 5.30; N, 13.50; Cu, 14.01. Calc.: C, 41.10; H, 5.29; N, 12.78; Cu, 14.50% .

$[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{CH}_3)_2](\text{ClO}_4)_2$ , [**Comp. 4**]; Found: C, 38.30; H, 3.90; N, 13.10; Cu, 15.68. Calc.: C, 38.05; H, 4.67; N, 13.65; Cu, 15.49 %.

$[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{C}_2\text{H}_5)_2](\text{ClO}_4)_2$ , [**Comp. 5**]; Found: C, 39.30; H, 5.00; N, 12.90; Cu, 15.18. Calc.: 39.63, H, 4.99; N, 13.20; Cu, 14.98 %.

$[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{C}_3\text{H}_7)_2](\text{ClO}_4)_2$ , [**Comp. 6**]; Found: Cu, 14.54. Calc.: 14.50 %.

### Physical measurements

C, H, N and Cu measurements were made in Chemistry Department of Tarbiat Modarres University. Electronic spectra were determined on a Unicam UV/VIS Spectrometer UV/2 spectrophotometer. FTIR spectra were recorded in the 4000–250  $\text{cm}^{-1}$  range as KBr disks using FTIR Galaxy Series FT-IR 5000 Unicam England. The spectra were calibrated using polystyrene bands at 3028, 1601, and 1208  $\text{cm}^{-1}$ . Magnetic susceptibilities were performed in 5–265 K range on a Manics DSM–8 susceptometer by the Leiden

Institute of Chemistry, niversity, The Netherlands. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal Constants [18].

## RESULTS AND DISCUSSION

### Electronic Spectra

The spectroscopic data for all complexes is presented in Table 1. The electronic spectra of all compounds were obtained in  $\text{CHCl}_3$  and are very similar, illustrating similar geometry. All complexes show a broad band appearing in 540 to 640 nm range, due to a d-d transition of copper(II) ion and is in agreement with asymmetric planar or tetragonal arrangement of ligands around it [19-21]. The second absorption band at about 300 nm., is assigned to charge transfer from the non-bonding orbital of bridging oxygen atoms to half-filled  $\text{dx}^2\text{-y}^2$  orbital of copper(II) ion [22,23]. The final absorption band at 235 nm is associated with  $\pi \rightarrow \pi^*$  transition of aromatic part of ligand [24].

### Magnetic properties

The magnetic moment of all complexes in  $\text{CHCl}_3$  at room temperature were found to be 1.16 to 1.77 BM range per copper which appears to be low for a  $\text{d}^9$  configuration, so there must be a strong spin-spin interaction through the bridging ligands [25-28]. The magnetic susceptibility of a powdered sample of complex  $[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{CH}_3)_2](\text{ClO}_4)_2$  was measured on a fully automatized Manics DSM-8 susceptometer from 5 to 265 K. The susceptibility data were corrected for the diamagnetism of constituent using Pascal

Constants [18]. The magnetic susceptibility data and the calculated parameters are shown in Table 2. The magnetic properties of the complex are given in Figure 1 in form of  $\chi_{\text{Cu}}$  versus T. The data were fitted to modified Bleaney-Bowers equation for two interacting  $S = 1/2$  centers [29].

$$\chi_m = (2N^2g^2\beta^2 / kT)[3 + \exp(-2J/kT)]^{-1}(1-\rho) + \chi_p \times \rho \quad (1)$$

$$H_{\text{ex}} = -2JS_1S_2 \quad (2)$$

The fit was accomplished by means of a non-linear least-square procedure. The factor J is defined by Hamiltonian (2). N, g,  $\beta$ , k and T have their usual meaning. The parameter  $\rho$  denotes the fraction of paramagnetic impurity in the sample. The data show a maximum in the  $\chi_{\text{Cu}}$  versus T curve at about 100 K in the temperature available and fit the above expression very well with  $2J = -126 \text{ cm}^{-1}$ ,  $g = 2.03$  and  $\rho = 2.16 \times 10^{-2}$ .

### Infrared spectra

The IR spectra of free ligands and complexes were obtained in the  $4000\text{--}250 \text{ cm}^{-1}$  range. The spectra were studied in some detail, given the symmetry of the molecules. For  $\text{Cu}_2\text{O}_2\text{L}_4$  kind of compounds with  $\text{D}_{2h}$  symmetry, 18 normal modes of vibration can be expected, 8 of which are IR active and they are:  $3\text{B}_{1u}$ ,  $2\text{B}_{2u}$  and  $3\text{B}_{3u}$ . Two important modes of  $\text{B}_{2u}$  and  $\text{B}_{3u}$  associate with vibration of  $\text{Cu}_2\text{O}_2$  unit are to be expected; this could be of great help in verifying the dinuclear structure of the complex [30-34]. The frequency of this modes is affected by the  $\text{Cu}_2\text{O}_2$  planarity and the angle of

Fig. 1: A plot of  $\chi_{\text{Cu}}$  versus T for  $[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{CH}_3)_2](\text{ClO}_4)_2$  Complex.

Fig. 2: A plot of  $\chi_{\text{Cu}} \times T$  versus T for complex  $[\text{Cu}_2(\text{A5PIC})_4(\text{O}-\text{CH}_3)_2](\text{ClO}_4)_2$  Complex.

Table 1: Spectroscopic data for all complexes

Complex	IR (cm <sup>-1</sup> ) Anion	IR (cm <sup>-1</sup> ) Cu-O	UV-Vis. (nm)	$\mu_{Cu}$ (R.T.) BM
[Comp. 1]	1091, 627	500, 547	594, 294, 236	1.16
[Comp. 2]	1091, 627	513, 547	540, 294, 236	1.77
[Comp. 3]	1089, 626	515, 547	598, 296, 236	1.58
[Comp. 4]	1101, 624	534, 563	624, 312, 234	1.67
[Comp. 5]	1093, 627	511, 536	642, 306, 236	1.20
[Comp. 6]	1109, 627	511, 563	581, 310, 236	1.56

Table 2: Magnetic susceptibility data and calculate parameters for complex [Cu<sub>2</sub>(ASPIC)<sub>4</sub>(O-CH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

Temp. (K)	$\chi_{Cu} \times 10^{+3}$	Temp. (K)	$\chi_{Cu} \times 10^{+3}$	Temp. (K)	$\chi_{Cu} \times 10^{+3}$	Parameters
263.42	1.017	161.92	1.341	57.92	2.689	-2J = 126 cm <sup>-1</sup>
258.69	1.124	157.02	1.328	53.02	2.856	g = 2.03
255.96	0.8710	152.12	1.242	47.57	3.030	$\rho = 2.16 \times 10^{-2}$
251.41	0.9277	147.16	1.308	45.23	3.196	
246.56	1.032	142.05	1.232	42.15	3.375	
241.84	1.050	137.19	1.303	39.16	3.548	
237.20	1.029	132.29	1.384	36.42	3.858	
232.11	1.048	127.05	1.365	33.67	4.037	
227.16	1.038	122.26	1.287	30.13	4.422	
222.14	1.053	117.56	1.487	27.62	4.844	
217.19	0.9985	112.63	1.407	25.15	5.222	
212.24	1.053	107.65	1.596	21.37	5.912	
206.97	1.145	102.49	1.584	18.20	6.468	
201.70	1.138	97.41	1.686	17.77	7.096	
196.94	1.095	92.59	1.787	14.75	7.773	
192.31	1.109	87.91	1.832	13.01	8.613	
187.03	0.9860	82.59	1.808	11.40	10.70	
181.82	1.119	77.92	2.065	8.46	13.52	
177.23	1.279	72.67	2.278	7.33	17.732	
171.94	1.237	68.12	2.249	5.24	20.81	
166.96	1.073	62.52	2.396	4.87	21.65	

Cu-O-Cu units [35]. The IR spectrum of all complexes were compared with that of the free ligand. In fact all of the bands that are present in the free ligand are also observed in the spectrum of the complex. In addition, bands observed at  $\approx 1110$ , and  $626 \text{ cm}^{-1}$  for all of complexes, which can assigned to the non-coordinated perchlorate anion [36]. All compounds exhibit two bands

in the  $500$  to  $570 \text{ cm}^{-1}$  range and can be attributed to copper - oxygen antisymmetric and symmetric ring vibrations [37].

## CONCLUSION

In summary, six alkoxo-bridge dinuclear copper(II) complexes (1)–(6) have been made in one-step synthesis

and spectroscopically characterized. All compounds show a subnormal magnetic moment between 1.16 to 1.77 BM per copper at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule.

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