

## Preparation, Spectroscopic and Magnetic Characterization of Di- $\mu$ -methoxy-bis(2-amino-3-methylpyridine)<sub>2</sub> copper(II) with NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>

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**Summary:** Three new dinuclear copper(II) complexes of 2-amino-3-methylpyridine has been prepared and characterized by spectroscopic, magnetic and elemental analysis. Complex [Cu<sub>2</sub>(2-amino-3-methylpyridine)<sub>4</sub>(OCH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> were characterized magnetically by magnetic susceptibility. The magnetic susceptibility of powdered [Cu<sub>2</sub>(2-amino-3-methylpyridine)<sub>4</sub>(OCH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> has been examined in the range of 5 to 270 K. The dimer exhibits an antiferromagnetic exchange interaction. The best fit to the Bleaney-Bowers equation was obtained yielding  $2J = 133 \text{ cm}^{-1}$  with  $g = 2.02$  and  $p = 2.58 \times 10^2$  for the complex in c.g.s. units. The dinuclear complexes are ESR silent in solid state and only a weak signal of monomeric impurities is observed. Frozen solution ESR spectra suggests that the complexes dissociate when dissolved in DMF or DMSO.

### Introduction

The structural and magnetic properties of many dinuclear compounds containing Cu<sub>2</sub>O<sub>2</sub> system have been investigated previously in order to explain the influence of spin-spin interaction through the bridging system [1-6]. It is now generally accepted that the spin coupling in these complexes occurs through the bridging groups by a pathway in square-planar oxygen-bridged compounds of the type [Cu<sub>2</sub>(L)<sub>4</sub>(OR)<sub>2</sub>]<sup>2+</sup>, where (L = monodentate ligand). It is found that the isotropic exchange parameter,  $2J$ , is linearly related to the Cu-O-Cu bridging angle,  $\phi$ , [1,2] and this correlation has been explained in terms of molecular-orbital theory [7]. It should be noted, however, that while  $\phi$  is very important, but it is not the only structural parameter which can affect the value of  $2J$ . Sinn and co-workers [8-11] have demonstrated that the distortion from planar towards tetrahedral environment at the metal center also markedly affect the magnitude of  $2J$ , although they may not change its sign [12]. Another factor contributing to the magnitude of  $2J$  is the effect of changing the electron density at the bridging atoms [13]. Four decades ago, McWhinnie reported [14,15] the magnetic moment of a series of alkoxide-bridged complexes of the type [Cu<sub>2</sub>(ap)<sub>4</sub>(OR)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, where (ap = 2-aminopyridine). Unfortunately, no structural and magnetic studies information is available for these complexes. Several investigations have been performed on alkoxo-bridged complexes of the type [CuX(OR)]<sub>2</sub> where (ROH = an aminoalcohol and X = a uninegative ligand such as Br) [16,17]. In this series no linear relationship between  $\phi$  and  $2J$  value

has been found, presumably because in some of these complexes the Cu<sub>2</sub>CO<sub>2</sub> chelates are strongly distorted from planarity while in others the neighboring dimeric units are so close that they are able to form tetramers [18]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the Cu(II)-Cu(II) coupling in these systems is still imperfect. We are interested in the effect of different anions with the change in the magnetic properties. In the present study three dinuclear complexes of Cu(II) with 2-amino-3-methylpyridine (hereafter abbreviated as L) with the general formula [Cu<sub>2</sub>(L)<sub>4</sub>(O-CH<sub>3</sub>)<sub>2</sub>](X)<sub>2</sub>, where X = NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> are reported.

### Results and Discussion

The spectroscopic data for all complexes is presented in Table-1. All methoxy-bridged dimeric complexes have bands at about  $17 \times 10^3 \text{ cm}^{-1}$ , due to ligand field transitions for a CuN<sub>2</sub>O<sub>2</sub> chromophore [5,20]. In addition a second strong and sharp band is found for all these complexes at about  $25 \times 10^3 \text{ cm}^{-1}$ , which is characteristic for dinuclear copper(II) compounds with a square-planar Cu<sub>2</sub>N<sub>4</sub>O<sub>2</sub> chromophore, and has been assigned to charge transfer of bridging oxygen atoms to vacant copper(II) d orbitals [21]. The absorption band higher than  $34 \times 10^3 \text{ cm}^{-1}$  arises from  $\pi$ - $\pi^*$  transition of the ligand [22].

The infrared spectra of the present complexes, specially regarding the Cu<sub>2</sub>O<sub>2</sub> chelate and anion

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Table-1: Spectroscopic data for the complexes

Complex	Absorption spectra ( $10^3 \text{ cm}^{-1}$ )	IR ( $\text{cm}^{-1}$ ) ligand	IR ( $\text{cm}^{-1}$ ) anion	IR ( $\text{cm}^{-1}$ ) Cu-O	ESR powder	ESR (solution) DMF	$\mu_{\text{Cu}}$ (R.T.) BM
1	18.3, 26.4 34.6	3491, 3342 3193, 2936 1620-1000 776	1092, 1002 919, 624	514, 466	$g_{\text{av}}=2.07$	$g_{\parallel} = 2.31$ $g_{\perp} = 2.07$ $A_{\parallel} = 160$ $A_{\text{N1}} = 15$	1.27
2	17.2, 25.0 34.5	3491, 3342 3193, 2936 1620-1000 776	1384, 826 760	574, 517	$g_{\text{av}}=2.07$	$g_{\parallel} = 2.31$ $g_{\perp} = 2.07$ $A_{\parallel} = 160$ $A_{\text{N1}} = 15$	1.33
3	16.0, 24.8	3491, 3342 3193, 2936 1620-1000 776	1256, 1165 1030, 760	531, 469	$g_{\text{av}}=2.07$	$g_{\parallel} = 2.30$ $g_{\perp} = 2.07$ $A_{\parallel} = 156$	1.19

vibrations, are of particular interest. So far for square-planar-Cu-alkoxo bridged complexes, Cu-O vibrations are reported from 450-580  $\text{cm}^{-1}$  [14,23,24]. Examination of the infrared spectra of the present complexes reveal  $\text{Cu}_2\text{O}_2$  vibrations between 530-460  $\text{cm}^{-1}$  for these compounds [25,26]. The bands due to ionic perchlorate at 1092 (vs), 919(s) 1002 (s) and 624 (vs)  $\text{cm}^{-1}$  are assigned as the IR allowed  $\nu_3$  mode IR forbidden  $\nu_1$  mode and non-degenerate  $\text{ClO}_3$  symmetrical bending frequency  $\nu_4$ , respectively [27]. The bands at 1384 (va), 826 (s) and 760 (s)  $\text{cm}^{-1}$  are attributed to ionic nitrate for  $\nu_3$ ,  $\nu_2$  and  $\nu_4$ , respectively [28]. A comparison of IR of complex 3 with the free ligand, reveals the IR vibrations of 1256 (vs), 1165 (s), 1030 (vs) and 760 (vs)  $\text{cm}^{-1}$  are due to uncoordinate triflate anion [29,30]. The IR spectra of the free ligand shows two bands at 3491 (vs) and 3342 (vs)  $\text{cm}^{-1}$ . These bands are assigned to -NH vibrations. The bands at 3193 (vs) and 2936 (s)  $\text{cm}^{-1}$  are attributed to -CH aromatic and -CH aliphatic vibrations respectively. The region 1620-1000  $\text{cm}^{-1}$  contains many absorption caused by bending vibration as well as absorptions caused by C-C and C-N stretching vibration. As there are many more bending vibrations in a molecule than stretching vibrations, this region of the spectrums are particularly rich in absorption bands and shoulders. A band at 776(s)  $\text{cm}^{-1}$  is assigned to -CH out of plane deformation.

The X-band ESR spectra of all complexes were recorded at liquid nitrogen and room temperatures. In solid state, the complexes are ESR silent and only a weak signal of monomeric impurity are obtained near  $g_{\text{ave}} = 2.07$ . Such a diamagnetic EPR silent behaviour is reported in literature [31].

The observed frozen solution (77K) ESR spectrum of compounds is typical for mononuclear copper(II) complexes and have a  $g_{\parallel}$  values of 2.07 and  $g_{\perp}$  of 2.31 with  $A_{\parallel}$  value of about 160 G and  $A_{\text{N1}}$  of 15 G, this is a typical for mono-nuclear tetragonal copper(II) complexes with  $d_{x^2-y^2}$  ground state [15].

The magnetic susceptibility of a powdered sample of complex 2 was measured between 5-270 K. The susceptibility data were corrected for diamagnetism of sample holder and the constituent atoms by Pascal's constants. The magnetic properties of the complex illustrated in Fig. 1 in the form of  $\chi_{\text{Cu}}$  versus  $T$ . The data are given in Table-2 and fitted to the modified Bleaney-Bowers equation [32] for two interacting  $S = 1/2$  centers.

$$\chi_{\text{Cu}} = (2Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1}(1-p) + \chi_p \times p \quad (1)$$

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

The fit was accomplished by means of a non-linear least-squares procedure, *N.g.*  $\beta$ ,  $k$  and  $T$  have their usual meanings. The parameter  $p$  denotes the percentage of paramagnetic impurity in the sample. The singlet-triplet energy gap ( $-2J$ ) is defined by Hamiltonian (2). The data show a maximum in the  $\chi_{\text{Cu}}$  versus  $T$  curve at about 100 K in the temperature range available, and fit the expression (1) very well with  $2J = -133 \text{ cm}^{-1}$ ,  $g = 2.02$  and  $p = 2.58 \times 10^{-2}$  c.g.s. units. All complexes are known to be dinuclear with the room temperature magnetic moment between 1.19-1.27 BM per copper, which is lower for a  $d^9$  system. However, it is observed that as the temperature is lowered, the magnetic moments decreased. Thus, this behaviour supports the

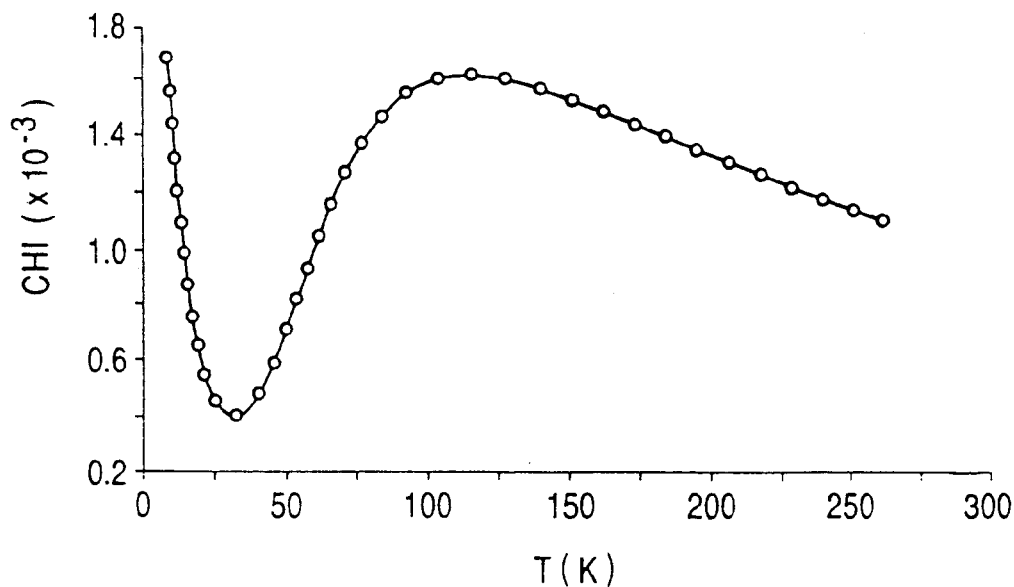


Fig. 1: A plot of  $\chi_{cu}$  versus  $T$  for  $[Cu_2(L)_4(OCH_3)_2](NO_3)_2$

Table-2: Magnetic susceptibility data and calculated parameters of complex  $[Cu_2(L)_4(OCH_3)_2](NO_3)_2$

Temp. (°K)	$\chi_{found} \times 10^{-3}$	Temp. (°K)	$\chi_{found} \times 10^{-3}$	Parameters
262.22	1.172	106.46	1.698	$J = -66.5 \text{ cm}^{-1}$
261.14	1.214	101.90	1.705	$g = 2.02$
255.96	1.242	98.00	1.735	$p = 2.58 \times 10^{-2}$
250.33	1.202	91.91	1.687	
247.24	1.271	86.87	1.751	
241.67	1.272	81.97	1.547	
238.85	1.329	77.40	1.242	
232.93	1.243	72.83	1.166	
226.99	1.176	67.76	1.089	
221.45	1.304	62.69	0.8802	
216.68	1.336	57.75	0.8247	
211.56	1.358	52.93	0.7713	
206.46	1.412	47.92	0.6800	
201.36	1.390	45.41	0.6465	
196.26	1.422	42.57	0.7079	
191.81	1.536	39.16	0.6321	
186.69	1.449	36.42	0.4601	
181.49	1.516	33.42	0.6077	
176.70	1.476	30.64	0.5997	
171.24	1.493	27.18	0.5297	
166.96	1.416	24.45	0.5340	
161.75	1.546	21.20	0.5326	
156.52	1.562	18.97	0.6258	
151.27	1.568	16.88	0.7655	
145.97	1.595	15.09	0.6213	
140.88	1.690	13.54	0.8189	
136.18	1.520	9.33	0.9287	
130.92	1.633	9.24	0.9261	
127.40	1.670	7.08	1.034	
122.69	1.787	5.78	1.350	
116.03	1.648	5.60	1.247	
111.80	1.702			

presence of antiferromagnetic spin-spin interaction through the bridging system.

## Experimental

### Chemicals

All chemicals were of reagent grade quality, purchased from Merck Chemical Company and used as received without further purification.

### Synthesis of $[Cu_2(L)_4(O-CH_3)_2](ClO_4)_2$ 1

The complex 1 was prepared by adding 1 mmol of copper(II) perchlorate hexahydrate to a stirring solution of 2 mmol ligand L in 50 ml of methanol. After a week, the violet crystals filtered, washed with methanol and air dried. Yield  $\approx$  65%. Anal. Calcd.  $Cu_2C_{26}H_{38}N_8Cl_2O_{10}$ : C, 38.05; H, 4.66; N, 13.66; Cu, 15.49%. Found: C, 39.45; H, 4.67; N, 13.71; Cu, 15.72%.

### Synthesis of $[Cu_2(L)_4(O-CH_3)_2](NO_3)_2$ 2 and $[Cu_2(L)_4(O-CH_3)_2](CF_3SO_3)_2$ 3

The complexes 2 and 3 were obtained by a similar method as described for 1, using copper(II) nitrate trihydrate and copper(II) triflate. Yield  $\approx$  68% and 63% for 2 and 3 respectively. Anal. Calcd. for  $Cu_2C_{26}H_{38}N_{10}O_8$  (2): C, 41.88; H, 5.14; N, 18.78;

Cu, 17.04%. Found: C, 41.11; H, 5.14; N, 18.04; Cu, 17.32%. Anal. Calcd. for  $\text{Cu}_2\text{C}_{28}\text{H}_{38}\text{N}_8\text{O}_3\text{F}_6$  (3): C, 36.56; H, 4.16; N, 12.18; Cu, 13.82%. Found: C, 36.10; H, 4.02; N, 12.58; Cu, 13.67%.

#### Physical measurements

C, H and N determinations were obtained from the Microanalytical Laboratory of University College, Ireland. Cu determination were carried on a Perkin-Elmer 2380 Atomic Absorption spectrophotometer. Electronic spectra of solid compounds were determined on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. The FTIR spectra of complexes as KBr discs were performed in the range of 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer. X-band electron paramagnetic resonance spectra were recorded of the powder and frozen solutions of the complexes, both at room and liquid nitrogen temperatures in DMF or DMSO on a Jeol RE2x electron spin resonance spectrometer using DPPH ( $g = 2.0036$ ) as a standard. Magnetic susceptibilities were measured in the temperature ranges 5-270 K with a fully automatized Manics DSM-8 susceptometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal's contents [19]. A magnetic susceptibility balance of Johnson Matthey Alfa Products was used to measure the room temperature magnetic moment.

#### Conclusions

With the present experimental data, three new bis-( $\mu$ -methoxy)-bridged dinuclear copper(II) complexes have been synthesized. All complexes show lower magnetic moments between 1.19-1.27 BM per copper(II), suggesting strong spin-spin interaction through bridging system. The singlet-triplet energy gap ( $2J$ ) of  $-133 \text{ cm}^{-1}$  were calculated for the complex 2. The X-band ESR spectrum of all complexes in DMF or DMSO glass (77K) show  $g_1 = 2.07$ ,  $g_2 = 2.31$  with  $A_1$  of about 160 G and  $A_{N1} = 15$  G, which is typical of monomeric tetragonal copper(II) complex with  $D_{x_2-y_2}$  ground state.

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#### References

1. D.J. Hodgson, *Progr. Inorg. Chem.*, **19**, 173 (1975).
2. E.D. Estes, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **13**, 1654 (1974).
3. H. Okawa, M. Koikawa and S. Kida, *J. Chem. Soc. Dalton Trans.*, 469 (1990).
4. J. van Konongbruggen, E. Muller, J.P. Haasnoot and J. Reedijk, *Inorg. Chim. Acta.*, **208**, 37 (1993).
5. G.A. van Albada, M.T. Lakin, N. Veldman, A.L. Spek and J. Reedijk, *Inorg. Chem.*, **34**, 4910 (1995).
6. G.A. van Albada, W.J.J. Smeets, A.L. Spek and J. Reedijk, *Inorg. Chim. Acta*, **260**, 151 (1997).
7. W.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson and W.E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).
8. P. Gluvchinsky, G.M. Mockler, P.C. Healy and E. Sinn, *J. Chem. Soc. Dalton Trans.*, 1156 (1974).
9. R.M. Countryman, W.T. Robinson, and E. Sinn, *Inorg. Chem.*, **13**, 2013 (1974).
10. E. Sinn, *J. Chem. Soc. Chem. Commun.*, 665 (1975).
11. E. Sinn, *Inorg. Chem.*, **15**, 358 (1976).
12. D.J. Hodgson, *Inorg. Chem.*, **15**, 3174 (1976).
13. P.J. Hay, J.C. Thibeault and R. Hoffman, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
14. W.R. McWhinnie, *J. Chem. Soc.*, 2959 (1964).
15. W.R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965).
16. E.D. Estes and D.J. Hodgson, *Inorg. Chem.*, **14**, 334 (1975).
17. J.A. Bertrand and P.G. Eller, *Progr. Inorg. Chem.*, **21**, 29 (1976).
18. R. Mergehenn, L. Merz and W. Haase, *Acta Cryst.*, **B22**, 505 (1976).
19. I.M. Kolthoff and P.J. Elving, in *Treatise on Analytical Chemistry*, Vol. 4, part 1 (Interscience Publ. New York, 1963).
20. A. Bencini, D. Gatteschi, C. Zanchini and W. Hasse, *Inorg. Chem.*, **24**, 3485 (1985).
21. S. Kida, Y. Nishida and M. Sakamoto, *Bull. Chem. Soc. Jpn.*, **46**, 2428 (1973).

22. T. Lidgren and K. Pilaya, *Inorg. Chim. Acta.* **73**, 153 (1983).
23. F. Demartin, M. Manussero, L. Naldini, A. Panzanelli and M.A. Zoroddu, *Inorg. Chim. Acta.*, **171**, 229 (1990).
24. M. Drillon, A. Grand and P. Rey, *Inorg. Chem.*, **29**, 771 (1990).
25. J.R. Ferraro, in *Low Frequency Vibrations of Inorganic and Coordination Compounds*; Plenum Press: New York, (1971).
26. E. Ghomashchi, *Spectrosc. Lett.*, **27**, 829 (1994).
27. Z.L. Lu, C.V. Duan, Y.P. Tian, X.Z. You, H.K. Fun and X.Y. Huang, *Inorg. Chem.*, **35**, 2335 (1996).
28. B.J. Hathaway, D.G. Holah and M. Hudson, *J. Chem. Soc.*, 4586 (1963).
29. T. Otieno, S.J. Rettig, R.C. Thompson and J. Trotter, *Can. J. Chem.*, **67**, 1964 (1989).
30. J.S. Haynes, S.J. Rettig, J.R. Sams, R.C. Thompson and J. Trotter, *Can. J. Chem.*, **64**, 429 (1986).
31. M.G.B. Drew and P.C. Yates, *J. Chem. Soc. Dalton, Trans.*, 2995 (1988).
32. B. Bleaney and K.D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).