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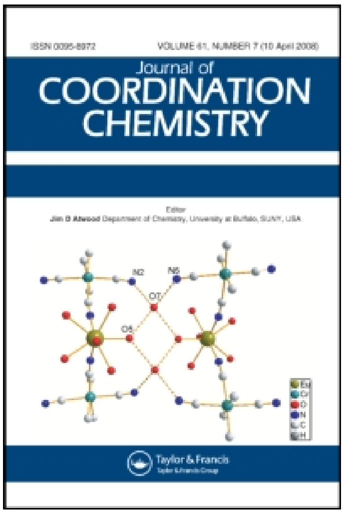

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Synthesis and characterization of two acetato-bridged dinuclear copper(II) complexes with 4-bromo-2-((4 or 6-methylpyridin-2-ylimino)methyl)phenol as ligand

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First published on: 12 October 2009

To cite this Article Hasanvand, Farshideh , Hoseinzadeh, Ali , Zolgharnein, Javad and Amani, Saeid(2010) 'Synthesis and characterization of two acetato-bridged dinuclear copper(II) complexes with 4-bromo-2-((4 or 6-methylpyridin-2-ylimino)methyl)phenol as ligand', Journal of Coordination Chemistry, 63: 2, 346 — 352, First published on: 12 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903330294

URL: http://dx.doi.org/10.1080/00958970903330294

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Journal of Coordination Chemistry
Vol. 63, No. 2, 20 January 2010, 346–352

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Synthesis and characterization of two acetato-bridged dinuclear copper(II) complexes with 4-bromo-2-((4 or 6-methylpyridin-2-ylimino)methyl)phenol as ligand

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(*Received 26 July 2009; in final form 27 July 2009*)

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The synthesis and characterization of two new acetato-bridged dinuclear copper(II) complexes are described. Both compounds have the general formula $[Cu(L)(\mu\text{-}O_2C\text{–}CH_3)]_2$, in which L = 4-bromo-2-((4-methylpyridin-2-ylimino)methyl)phenol or 4-bromo-2-((6-methylpyridin-2-ylimino)methyl)phenol. The title compounds consist of dinuclear units with bridging acetato groups and a ligand linked to each copper *via* the phenol oxygen and nitrogen. Both compounds were synthesized in a one-step reaction and characterized by elemental analysis, Fourier transform infrared (FTIR), electron spin resonance (ESR), and electronic spectra and by room temperature magnetic moments. The compounds exhibit antiferromagnetic interactions at room temperature. UV-Vis spectra show four absorptions attributed to d–d transitions of copper, ligand → metal charge transfer and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of ligand. The FTIR spectra indicate a $Cu_2O_4C_2$ ring vibration. Both complexes show room temperature magnetic moments of about 1.6 B.M. per copper. The X-band ESR studies indicate a weak half-field band, characteristic of the Cu(II)–Cu(II) dimer, observed at 1552 and 1558 G for the complexes, strongly suggesting that the hyperfine structure arises from a spin triplet species. The spectra of frozen samples in DMSO or DMF at liquid nitrogen temperature show a typical $\Delta m = 1$ transition.

Keywords: Dinuclear copper(II) complexes; Spin–spin interaction; Diacetato-bridged

1. Introduction

A fascinating field of research is the study of polynuclear complexes. Magnetic properties of a polynuclear complex of paramagnetic metal ions are, in general, different from the sum of the magnetic properties of each metal ion fragment separately [1]. Bleaney and Bowers [2] demonstrated that the magnetic behavior of copper(II) acetate monohydrate was due to the dinuclear nature and magnetic exchange interaction. Since then, exchange coupled polynuclear systems have seen exponential increase in publications [3–8]. Such interaction between metal centers lies at the center of widely separated areas, such as physics of magnetic materials and the role of polynuclear reaction sites in biological [9–12] and catalytic processes [13–16]. Dinuclear copper(II)

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958970903330294

complexes have relatively simple single-ion properties facilitating interpretation of magnetic data. The simplest bridging systems use monoatomic bridges, such as hydroxo [17], alkoxo [18], chloro [19], bromo [20], fluoro [21], and azido [22]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the copper(II)–copper(II) coupling is still imperfect. In the present study, two dinuclear copper(II) complexes are reported with 4-bromo-2-((4-methylpyridin-2-ylimino)-methyl)phenol or 4-bromo-2-(6-methylpyridin-2-ylimino)methyl)phenol (hereafter abbreviated L_1 and L_2, respectively), $[Cu_2(L_1)_2(O_2C–CH_3)_2]$ or $[Cu_2(L_2)_2(O_2C–CH_3)_2]$.

2. Experimental

2.1. *Chemicals*

All chemicals were of reagent grade quality purchased from Merck Chemical Company and used as received.

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2.2. *Physical measurements*

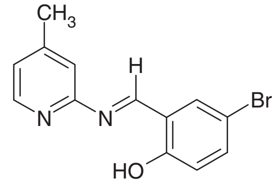
The C, H, and N determinations were made in the Research Institute of Petroleum Industry of Iran. Cu determination was carried out on a Perkin-Elmer 2380 Atomic Absorption spectrophotometer at 324.7 nm. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Fourier transform infrared (FTIR) spectra were made from 4000–250 cm^{-1} using a Galaxy 5000 spectrophotometer. Spectra were calibrated using polystyrene bands at 3028, 1601, and 1208 cm^{-1}. X-band electron paramagnetic resonance spectra were recorded on powder and frozen solutions at room and at liquid nitrogen temperatures in DMF or DMSO on an IBM electron spin resonance (ESR) spectrometer using DPPH ($g = 2.0036$) as a standard. A Johnson Matthey Alfa products magnetic susceptibility balance was used to measure the room temperature magnetic moments.

2.3. *Preparation of the ligands*

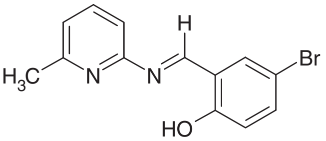
The ligands were prepared according to the following procedures.

2.3.1. 4-Bromo-2-((4-methypyridin-2-ylimino)methyl)phenol (L_1). 10 mmol 2-amino-4-methylpyridine in 15 mL methanol was added to 10 mmol 4-bromo-2-hydroxybenzaldeyhyde in 25 mL CH_3OH. By the addition of five drops concentrated H_2SO_4 and 2 h reflux, yellow precipitate separated was washed with hot methanol and air dried. Yield *ca* ≈ 96%. Elemental analysis for $C_{13}H_{11}N_2BrO$: Found (%): C, 52.65; H, 3.74; N, 9.87. Calcd (%): C, 53.36; H, 3.81; N, 9.62. ^1H NMR ($CDCl_3$, ppm): δ 2.28(s, $3H_{met.}$), 6.95–8.40(m, $6H_{aro.}$), 9.47(s, $1H_{imin.}$), 13.05(s, $1H_{phen.}$) (scheme 1).

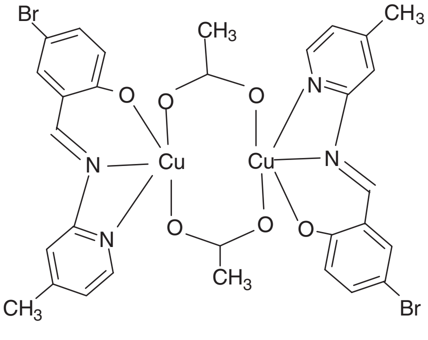
2.3.2. 4-Bromo-2-((6-methypyridin-2-ylimino)methyl)phenol (L_2). This compound was obtained by similar method as described for L_1. Yield *ca* ≈ 95%. Elemental analysis for



Scheme 1. Structure of ligand L_1.



Scheme 2. Structure of ligand L_2.



Scheme 3. Proposed structure for **1**.

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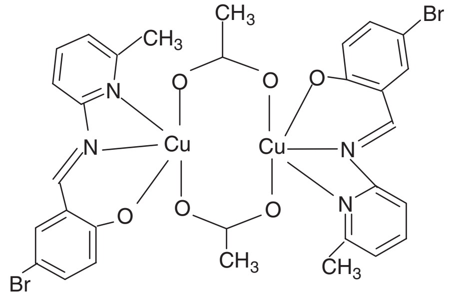
$C_{13}H_{11}N_2BrO$: Found (%): C, 54.58; H, 3.91; N, 9.50. Calcd (%): C, 53.36; H, 3.81; N, 9.62. ^{1}H NMR ($CDCl_3$, ppm): δ 2.66(s, $3H_{met.}$), 6.92–7.78(m, $6H_{aro.}$), 9.40(s, $1H_{imin.}$), 13.10(s, $1H_{phen.}$) (scheme 2).

2.4. *Preparation of the complexes*

Coordination compounds were prepared according to the following general procedure.

2.4.1. $[Cu_2(L_1)_2(\mu\text{-}O_2C–CH_3)_2]$ (1). 2 mmol ligand L_1 and 2 mmol triethylamine were dissolved in 25 mL methanol; 2 mmol $Cu(O_2C–CH_3)_2 \cdot H_2O$ was also dissolved in 50 mL CH_3OH. The Cu(II) salt solution was then added slowly to the ligand solution. After 4 h reflux, the brown precipitate separated and was washed with hot methanol and THF. Yield *ca* ≈ 55%. Elemental analysis for $C_{30}H_{26}Br_2O_6N_4Cu_2$: Found (%): C, 44.13; H, 3.44; N, 6.37; Cu, 15.73. Calcd (%): C, 43.65; H, 3.18; N, 6.79; Cu, 15.40 (scheme 3).



Scheme 4. Proposed structure for **2**.

Table 1. Spectroscopic data for **1** and **2**.

Complex	Absorption UV-Vis (nm)	IR (acetate) (cm^{-1})	IR(Cu–O) (Cu–N) (cm^{-1})	ESR half-field	ESR powder	ESR solution in DMF	μ_{Cu} (R.T.) B.M.
1	667, 418, 295, 270	1556, 1415	549, 464, 349, 279	$g_h = 4.36$	$g = 2.06$	$g_{\parallel} = 2.06$ $A_{\parallel} \approx 165$ $A_{n\perp} \approx 15$	1.58
2	671, 413, 292, 277	1527, 1381	534, 439, 354, 283	$g_h = 4.04$	$g = 2.06$	$g_{\parallel} = 2.07$ $A_{\parallel} \approx 160$ $A_{N\perp} \approx 15$	1.63

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2.4.2. $[Cu_2(L_2)_2(\mu\text{-}O_2C\text{–}CH_3)_2]$ (2). This complex was obtained by similar method as reported for **2**. Yield *ca* ≈ 45%. Elemental analysis for $C_{30}H_{26}Br_2O_6N_4Cu_2$: Found (%): C, 44.28; H, 2.97; N, 6.61; Cu, 16.22. Calcd (%): C, 43.65; H, 3.18; N, 6.79; Cu, 15.40 (scheme 4).

3. Results and discussion

3.1. *Electronic spectra*

Spectroscopic data for all compounds are presented in table 1. Electronic spectra of both complexes were obtained from a solid sample using diffuse reflectance and are very similar, illustrating similar geometry. The compounds show a broad band at 667 nm for **1** and 671 for **2** due to ligand field transition for a CuN_2O_3 chromophore [23, 24]. An absorption band at 418 nm for **1** and 413 nm for **2** are assigned to charge transfer from oxygen to $d_{x^2-y^2}$ orbital of copper(II) [23, 25]. The last two absorptions at 295 and 275 nm for both **1** and **2** are associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [26].

3.2. *Infrared spectra*

The infrared spectra of acetate and $Cu_2N_2O_2$ are of particular interest [27–34]. All bands present in the free ligand are also observed in the spectra of the complexes.

Figure 1. Frozen solution (77 K) ESR X-band for complex **1** in DMF.
*Denotes (diphenylpicrylhydrazine) DPPH marker ($g = 2.0036$).

Based on data from earlier reports [35, 36], we assign bands at 549 and 464 cm^{-1} and at 534 and 439 cm^{-1} (for **1** and **2**, respectively) to Cu–O vibrations. The bands at 349 and 279 cm^{-1} and at 354 and 283 cm^{-1} (for **1** and **2**, respectively) are assigned to Cu–N vibrations: however, these vibrations are likely coupled Cu–N and Cu–O vibrations. These data indicate L_1 is closer to copper(II) than L_2 due to the steric effect of methyl ortho to nitrogen in L_2. The bridging acetate in **1** has higher Cu–O vibration energy in **2** consistent with shorter Cu–Cu distance in **1** than in **2**.

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3.3. *Magnetic moment and ESR*

Both complexes are dimeric with room temperature magnetic moments of 1.58 and 1.63 B.M. per copper for **1** and **2**, respectively, low for a d^9 configuration from spin–spin interaction through the bridging ligands [37]. The spin–spin interaction in **1** is higher than in **2**, in agreement with data from IR spectra [8]. To provide further evidence for antiferromagnetic interaction, X-band powder and frozen solution ESR spectra were obtained at liquid nitrogen and at room temperatures. In the solid state, the spectra were similar and ESR silent with only a weak signal due to monomeric impurity ($g = 2.06$). Frozen solution ESR spectra of both compounds is typical for a dinuclear copper(II) complex. A weak $\Delta m = 2$ transition for both compounds confirms $\mathrm{Cu} \cdots \mathrm{Cu}$ magnetic exchange interaction at half-field (1552 G for **1** and 1558 G for **2**), which is characteristic of a dimer [2, 38, 39].

The $g_{\|}$ values of 2.06 and 2.07 (for **1** and **2**, respectively) with $A_{\|} \approx 162$ G is in agreement with a $d_{x^2-y^2}$ ground state and a square-pyramidal geometry [40–43]. The A_N value of $\approx$15 G and the presence of seven peaks for nitrogen superhyperfine structure for the complexes agrees with two N donors per copper(II) (see figure 1 and Supplementary material).

4. Conclusion

Two new bis-(μ-alkoxo)-bridged dinuclear copper(II) complexes with 4-bromo-2-((4-methylpyridine-2-ylimino)methyl)phenol or 4-bromo-2-((6-methylpyridine-2-ylimino)-methyl)phenol as the ligands have been made in a one-step synthesis and spectroscopically characterized. Both complexes show subnormal magnetic moments between 1.58 and 1.63 B.M. per copper at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule. Data from IR spectroscopy show that L_1 is closer to copper(II) than L_2 due to the steric effect of methyl; the IR for bridging acetate is in agreement with the magnetic moments. The X-band ESR spectra of **1** and **2** with $g_{\parallel} = 2.06$ and $A_{\parallel} \approx 163\,\mathrm{G}$ are typical of dimeric square-pyramidal copper(II) complexes.

Acknowledgements

The authors would like to thank the Research Council of Arak University for financial support of this research. The authors also appreciate the Chemistry Institute and DAAD Organization in Chemnitz University in Germany for the services, facilities, and physical measurements.

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