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Synthesis and Magnetic Property of Binuclear Copper(II) and Nickel(II) Complexes of Biprotic Bridging Ligand H_2bspda

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Two binuclear complexes [MbspdaM(OAc)$_2$·nH$_2$O] (M = Cu(II), n = 1, **1**; M = Ni(II), n = 2, **2**, H_2bspda = N,N'-*bis*(salicyidene)-5,6-phenanthrolinenediamine, have been prepared and characterized by element analysis, IR, ^{1}H and ^{13}C NMR, UV-Vis and EI-MS analysis. Magnetic measurements showed that both binuclear complexes exhibit anti-ferromagnetic interaction between the binuclear centers with the coupling coefficient value J/k = -4.02 K and corresponding g = 2.12 for **1** and J/k = -0.318 K and the corresponding g = 1.98 for **2**.

Key Words: Schiff base, Binuclear copper(II)/nickel(II) complex, Magnetic property.

INTRODUCTION

Magnetic property of transition metal complexes is one of interesting fields in both chemistry and material science. Some small inorganic bridging ligands (such as *m*-hydroxo[1], *m*-azido[2] and *m*-oxalo[3] groups), as their flexible bonding ways, have been widely used to synthesize multinuclear complexes with short metal-metal distances and intriguing structural diversity. It was found in some metal complexes with similar bridging ligands or molds that the magnetic coupling coefficient (J) from two paramagnetic metal centers usually decreases with the increasing of distance between them, even vanishes completely. Organic bridging ligands with large π-conjugation system have been proved to be good candidates for constructing long metal-metal-distance multinuclear complexes and be able to offer intramolecular electro or energy transfers and show unique properties[4,5]. For example, π-conjugation Schiff base complexes can show excellent properties in asymmetric catalysis[6,7], phospho-aldol catalysis reaction[8], electroreduction of oxygen to water[9] and magnetic properties[10,11] and π-conjugation polypyridyl complexes have diverse electrochemical and photophysic properties[12]. With the interest in transition metal complexes we synthesized a biprotic bridging ligand with large π-conjugation system, N,N'-*bis*(salicyidene)-5,6-phenanthrolinenediamine (H_2bspda), which consists of both phenanthroline and salicylaldimine functional sites on the same molecule. Here we report the synthesis and magnetic properties of two binuclear complexes, [MbspdaM(OAc)$_2$·nH$_2$O] (M = Cu(II), n = 1, **1**; M = Ni(II), n = 2, **2**).

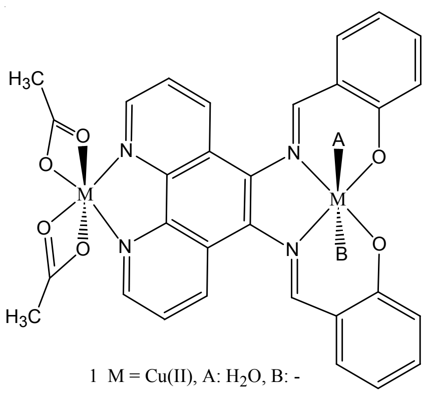
EXPERIMENTAL

Complexes copper(II)(bspda)copper(II)monoaquadiacetate (**1**) and nickel(II)-(bspda)nickel(II)diaquadiacetate (**2**) ware prepared from our early work[13a].

Detection method: Many attempting for growing single crystals did not success.

RESULTS AND DISCUSSION

Kasuga *et al.*[13b] synthesized two binuclear complexes $[(bpy)_2Ru(II)(bspda)$-$M(II)]\cdot 2ClO_4$ ($M = Ni^{2+}/Cu^{2+}$) by template reaction of 2-hydroxybenzaldehyde, Cu^{2+}/Ni^{2+} and ruthenium coordinated 5,6-diamine-1,10-phenanthroline[13c]. But the biprotic ligand (H_2bspda) was first synthesized through condensing 5,6-diamine-1,10-phenanthroline and 2-hydroxybenzaldehyde and corresponding metal salts[13a]. Binuclear copper(II)/nickel(II) complexes **1** and **2** were prepared by ligand with corresponding metal salts at the ratio of 1:2. EI-MS spectrum of complex **1** gives a very strong molecular ion peak at 601 (100 %) and a weak peak at 1082 (*ca.* 5 %). The former comes from the binuclear complex $[Cu(II)(bspda)Cu(II)(OAc)_2\cdot H_2O]$ and the later bellows to the impurity component (trinuclear complex) **1**· $[Cu(II)(OAc)_2$. Similar to complex **1** a small amount of impurity (*ca.* 5 %) of trinuclear complex **2**·$[Ni(II)(OAc)_2$ could also be found in complex **2**[13c]. In the IR spectrum the Δ value between asymm-carboxylato and symm-carboxylato is a useful tool for diagnosing the coordination mode of carboxylato group. A symmetrically bridging carboxylato group gives a Δ value smaller than 200 cm^{-1}, whereas an asymmetrically bridging one and mono-dentate one has a larger Δ value[14]. The infrared spectrum of **1** shows one smaller Δ value 155 cm^{-1} (asymm-carboxylato at 1576 cm^{-1} and symm-carboxylato at 1421 cm^{-1}) indicating that the two carboxylato group are equivalent and symmetrically bridging to the center copper atom. Similar to **1**, the Δ value in **2** is 158 cm^{-1} (asymm-carboxylato at 1576 cm^{-1} and symm-carboxylato at 1418 cm^{-1}). These explain their symmetrically chelating mode of the two carboxylato groups in **1** and **2**[15,16].



1 M = Cu(II), A: H_2O, B: -
2 M = Ni(II), A = B = H_2O

Fig. 1. Molecular structures of complex **1** and **2**

The absorption spectrum of the ligand (in DMF) shows intra-ligand charge transfer bands at 278 nm (ε, 22700 M^{-1} cm^{-1}) and 356 nm (ε, 15700 M^{-1} cm^{-1}). The absorption bands are shifted to 304 and 368 nm for **1**, 322 and 394 nm for **2**, respectively, as the LC transitions centered on the phenanthroline substituted Salen ligand. The sorption bands of **1** and **2** in the 250-300 nm region are contributed to the LC transitions centered on the carboxylato groups and the absorption bands of 444 for **1** and 486 nm for **2** exhibit the MLCT transitions[17]. This result suggests the presence of π-conjugation system between the phenanthroline ring and the Schiff base unit. The MLCT molar excitation coefficients of **1** and **2** are relatively weaker than that of their corresponding binuclear complexes, $[(bpy)_2Ru(II)(bspda)Cu(II)]\cdot 2ClO_4]$ and $[(bpy)_2Ru(II)(bspda)Ni(II)]\cdot 2ClO_4]$, which indicates that ruthenium(II) atom has a stronger exciting ability to the π-conjugation system than that of transition metal copper(II) and nickel(II) atoms.

TABLE-1
ELEMENTAL ANALYSIS AND UV-VIS SPECTRA OF
THE LIGAND AND ITS COMPLEXES

Compounds	Absorption λ_{max}/nm (ε/ 10^4 M^{-1} cm^{-1})	Ref.
*H_2bspda	278(2.3), 356(1.6)	This work
*1	254(0.6) 304(0.8), 368(0.5), 444(0.5)	This work
*2	268(1.3), 292(1.0), 322(0.8), 394(0.8), 486(0.3)	This work
**$[(bpy)_2Ru(II)(bspda)Cu(II)]\cdot 2ClO_4$	254(4.9), 287(9.2), 318(4.5), 349(2.7sh), 458(4.1)	14
**$[(bpy)_2Ru(II)(bspda)Ni(II)]\cdot 2ClO_4$	254(5.8), 288(8.0), 320(3.6sh), 340(2.7sh), 449(2.8).	14

Variable-temperature magnetic susceptibilities were measured on powder samples at a field of 2.0 T for **1** and 1.0 T for **2** in the temperature range 2-300 K. The temperature dependence of the magnetic susceptibility χ_M and of the product $\chi_M T$ for **1** is shown in Fig. 2. As the temperature decreases the χ_M value increases from 0.003 cm^3 mol^{-1} at room temperature to a maximum of 0.017 cm^3 mol^{-1} at 14.8 K. Below 14.8 K, the χ_M value decreases rapidly to a minimum 0.007 cm^3 mol^{-1} at 3.24 K and then increased continuously to 0.008 cm^3 mol^{-1} at 2.03 K. The overall magnetic behaviour of **1** is dominated by a bulk anti-ferromagnetic interaction between the spin carriers and resembles that of related binuclear copper(II) compounds[4d,18]. The $\chi_M T$ product at room temperature is about 0.74 cm^3 mol^{-1} K with the g factor 2.12, a value that is as expected for two magnetically isolated spin doublets (0.75 cm^3 mol^{-1} K)[19]. Upon cooling the $\chi_M T$ value decreases to 0.25 cm^3 mol^{-1} K at 14.8 K. Below 14.8 K, the $\chi_M T$ value decreases quickly down to 0.02 cm^3 mol^{-1} K at 2.03 K, The magnetic behaviours suggest that in **1** some anti-ferromagnetic interaction is predominant at intermediate temperatures[4d,18].

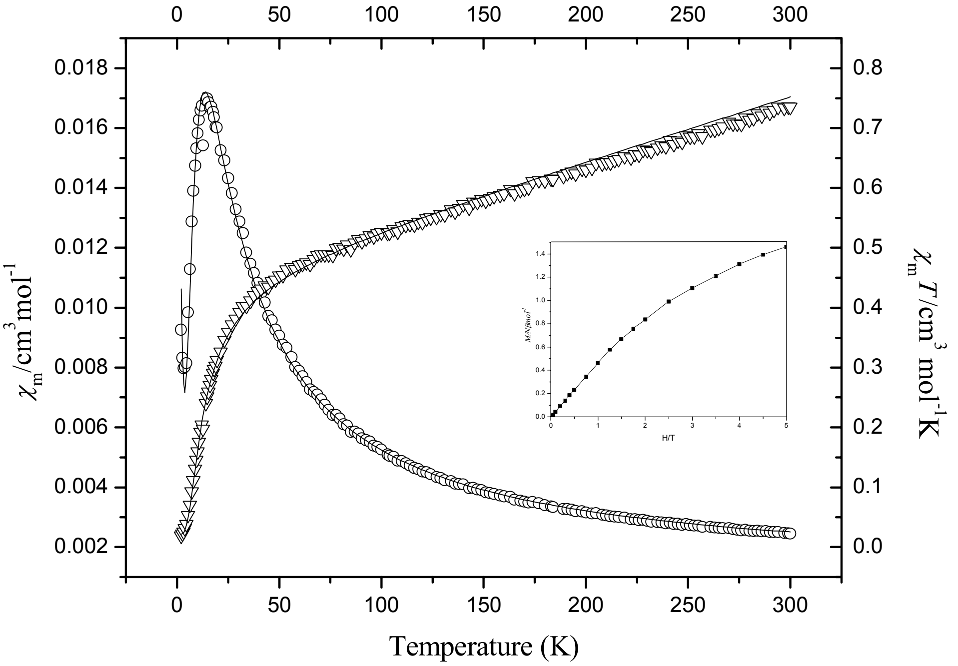


Fig. 2. Temperature dependence of χ_M and $\chi_M T$ for complex **1** measured at 2 T. The solid line corresponds to the best theoretical fit for the data in the 2-300 K and the M *versus* H plot

The temperature dependent bulk magnetic susceptibilities of compounds **1** was measured and interpreted as isolated antiferromagnetically coupled binuclear copper units. The magnetic system arises from the spin interactions between the two d^9 Cu(II) ions *via* the conjugated π-system of the bridging ligand, the so-called super-exchange mechanism. The experimental data were fitted by the Blealey-Bowers equation (1) for the isolated binuclear copper(II) complexes $(\hat{H} = -J \cdot \hat{S}_1 \cdot \hat{S}_2)$[20], which also accounts for impurities present in fraction and all symbols have their usual meanings.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{1}{[3 + \exp(-2J/kT)]} \times (1-\rho) + \frac{Ng^2\beta^2}{4kT} \times \rho + \chi_{tip} \qquad (1)$$

The best fit obtained from complex **1** led to the following parameters: J/k = -4.02 K. ρ = 0.04, g = 2.18, χ_{tip} = 60 × 10^{-6} and R = 9.5 × 10^{-4} (R = $\sum[(\chi_M)_{obs} - (\chi_M)_{caled}]^2 / \sum[(\chi_M)_{obs}]^2$). The negative value of J implies an anti-ferromagnetic exchange within the dimer. The reduced molar magnetization tends to 1.45 Nβ· for **1** when the fields approach 5 T and it is very far from the de Brillouin formula for two isolated Cu(II) ions. The feature is also indicative of the weak anti-ferromagnetic coupling in the compound.

The temperature dependence of the magnetic susceptibility χ_M and of the product $\chi_M T$ for 2 is shown in Fig. 3. The room temperature χ_M value is 0.007 cm^3 mol^{-1} and it increases with temperature, reaching a value of 0.234 cm^3 mol^{-1} at 2.0 K. The calculated room temperature $\chi_M T$ product is about 2.10 cm^3 mol^{-1} K, which is found to be higher than that of the two (S = 1) spin only value[21]. Upon cooling, the $\chi_M T$ value decreases with temperature to 21 K, showing an antiferromagnetic behaviour of nickel(II) dimer[3d]. In the temperature range of 10-21 K the $\chi_M T$ value decreases somewhat slowly and show an approximate plateau with an $\chi_M T$ value at about 0.93 cm^3 mol^{-1} K, which is in the expected range of Curie law of a spin doublet state. Below 10 K, the $\chi_M T$ value decreases quickly down to 0.47 cm^3 mol^{-1} K, showing a characteristic of an intramolecular antiferromagnetic interaction between the two single-ion triplet states[22].

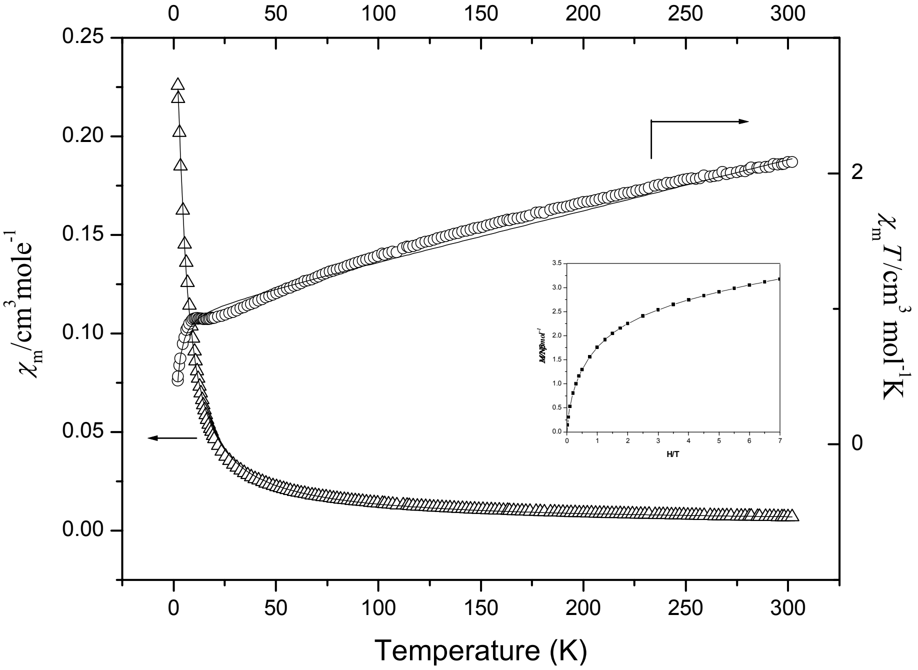


Fig. 3. Temperature dependence of χ_M and $\chi_M T$ for complex **2** measured at 1 T. The solid line corresponds to the best theoretical fit for the data in the 2-300 K and the M *versus* H plot of complex **2** measured at 1.83 K [(■) experimental data; (—) eye guide line]

To evaluate the intracluster super-exchange coupling constants in the title complex, a binuclear nickel(II) model including a mean field approach was used in equation (2), where J and parameters have the normal meanings.

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{[5 + \exp(-4J/kT)]}{[5 + 3\exp(-4J/kT) + \exp(-6J/kT)]} \times (1-\rho) + \frac{2Ng^2\beta^2}{3kT} \times \rho + \chi_{tip} \quad (2)$$

The experimental data were fitted and led to the following best parameters: J/k = -0.318 K, ρ = 0.042, g = 1.98, $\chi_{tip} = 40 \times 10^{-6}$ and R = 7.4×10^{-4} (R = $\sum[(\chi_M)_{obs} - (\chi_M)_{caled}]^2 / \sum[(\chi_m)_{obs}]^2$). The small negative value of J implies that there is weak antiferromagnetic interaction exchange between the metal centers in the dimer. The reduced molar magnetization tends to 3.18 Nβ· when the fields approach 7 T, which is lower than that from the de Brillouin formula for two isolated Ni(II) ions and also shows weak anti-ferromagnetic coupling for **2**.

Conclusion

In summary, the reason of antiferromagnetic interaction existed in the two binuclear complexes (**1** and **2**) from the intra-molecular magnetic-transfer through large π-conjugation system.

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