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# Two new end-on cyanato copper(II) complexes; synthesis, characterization, solvatochromism, magnetic investigation and quantum study

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ABSTRACT

The present paper deals with magnetic interactions, solvatochromism and DFT calculations of two new end-on cyanato-bridged dinuclear copper(II) complexes with the formula $[L(OCN)Cu(\mu_{N,N}\text{-}OCN)]_2$, **1** and **2**, where $L^1$ = *N,N*-dimethyl,-*N*′-benzyl-ethylenediamine (**1**) and $L^2$ = *N,N*-diethyl,-*N*′-benzyl-ethylenediamine (**2**). Both complexes were characterized on the basis of physicochemical and spectroscopic methods. X-ray crystallography of complex **2** showed a dinuclear nature with terminal and bridging cyanate groups. Each copper atom achieves a distorted square-pyramidal environment that is built up by five nitrogen atoms, with two nitrogen atoms coming from two N-bonded cyanato ligands that link two copper ions in an end-on fashion, one nitrogen atom from another cyanato ligand that acts as an N-bonded terminal ligand and the final two nitrogen atoms are from a chelating diamine ligand. The interaction between the two metal ions was investigated by magnetic measurements from 2 to 300 K. The variable temperature magnetic susceptibility data showed a weak ferromagnetic interaction with *J* values of 1.8 $cm^{-1}$ for **1** and 7.7 $cm^{-1}$ for **2**. DFT computational results buttressed the experimental observations. The positive solvatochromic behaviors of the compounds were investigated in some organic solvents. The spectral shifts of these solutes were correlated with Kamlet and Taft parameters (α, β and π*) using linear solvation energy relationships (LSEC). The multi-parametric analysis indicates that both the polarity/polarizability parameters (π*) and the hydrogen bond donating ability (β) of the solvents play an important role in the absorption maxima of the compounds.



## 1. Introduction

In the recent times, the study of magnetochemistry in dinuclear Cu(II) coordination compounds has been of interest due to the diverse structural and magnetic properties of these systems and, especially, because of the possibility to design structures that exhibit strong ferromagnetism. In addition, this dinuclear system is usually presented as an example of the simplest possible model for magnetic complexes since the Cu(II) ions in a $d^9$ electronic configuration have one unpaired electron per magnetic center. This feature allows one to search for a deeper understanding of ferro- and antiferromagnetic interactions. The key parameter in the design of the dinuclear complexes is to utilize appropriate bridging groups. Pseudo halide ligands, such NCO, $N_3$ and NCS, have received intense attention due to their extremely versatile bonding modes in transition metal chemistry that generate the rich structural variety of dinuclear complexes and their efficiencies in functioning in extending suitable super-exchange pathways between several paramagnetic centers. For two metal ions the most common bonding modes are: end-to-end (a) or an end-on mode (b, c) (Scheme 1). The end-on coordination mode is usually found in cyanato bridged dinuclear copper(II) compounds [1–9]. The magnetic properties of the majority of these compounds are based on the metal centers and bridging ligands properties, that is, on the nature of the magnetic orbitals and the bridging geometry. It was noted that a more quantitative approach is needed to fully understand the magnetic interaction to predict accurately the magnetic coupling constant, *J*. Therefore, computational studies, such as those using the DFT method, would be a useful approach in this regard.

In addition, copper(II) complexes have received considerable interest due to their solvatochromic properties. The effect of a solvent on the spectral properties of molecules is generally referred as

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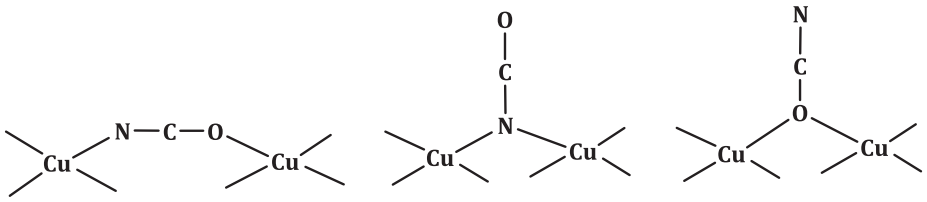



**Scheme 1.** Bridging modes of the cyanate ion.

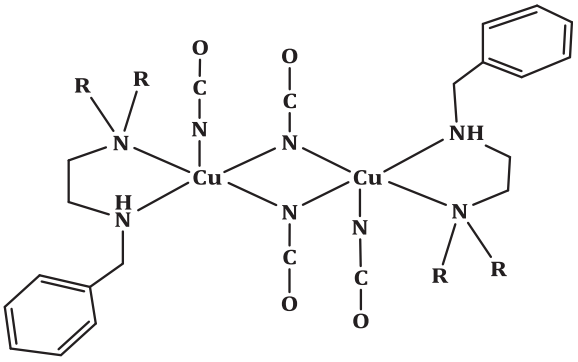
solvatochromism, and this has attracted much attention in chemistry and biology attributable to the potential applications as acid-base color indicators and optical sensors [10–12]. The solvent effect can be expressed by various empirical scales that are used to describe the solvatochromism behavior in metal complexes. Utilization of statistical software is very helpful for choosing the most important factor(s) that is responsible for the color change in different solvents. SPSS/PC software is a good choice in this regard that can correlate the experimental data to the empirical data [13–18].

This work follows from previous research focusing on dinuclear doubly bridged copper(II) compounds which showed intramolecular magnetic exchange phenomena and magneto-structural correlations [19]. As a continuation of our interest in dinuclear copper (II) complexes, we initiated an investigation on the copper(II) complexes with cyanato bridged ligands. We herein report two new doubly cyanato bridged dinuclear copper(II) compounds, abbreviated as $[L(NCO)Cu(\mu_{N,N}\text{-}OCN)]_2$, shown in (Fig. 1). Details of the synthesis, characterization and electronic properties of the compounds are reported. Also, values of the magnetic coupling constants extracted from magnetic susceptibility measurements are compared to theoretical calculations using a wide range of state of the art DFT methods.

## 2. Experimental

### 2.1. General

The ligand *N,N*-dimethyl,-*N′*-benzyl-ethylenediamine and *N,N*-diethyl,-*N′*-benzyl-ethylenediamine were prepared according to our published procedures [20,21]. All reagents and solvents were purchased from Merck and Aldrich and used without further purification.




R = $CH_3$, **1**
R = Et, **2**

**Fig. 1.** The complexes used in this study.

### 2.2. Preparation of the complexes

#### 2.2.1. $[L^1(NCO)Cu(\mu_{1,1}\text{-}NCO)]_2$, **1**

To an ethanolic solution (10 mL) of $Cu(OAC)_2{\cdot}2H_2O$ (0.198 g, 1 mmol) and the diamine ligand (0.178 g, 1 mmol) was added sodium cyanate (0.13 g, 1 mmol). The resultant mixture was stirred for 3 h at room temperature. The precipitate was filtered and washed with diethylether and dried. The compound was obtained as a blue solid with a typical yield of 31% (0.203 g). *Anal.* calc. for $C_{26}H_{36}Cu_2O_4N_8$ (MW = 651.72 g·mol$^{-1}$): C, 47.92; H, 5.57; N, 17.19; found: C, 47.73; H, 5.46; N, 17.07. Selected IR data ($\nu$/cm$^{-1}$ using KBr): 3448 (m, N—H str.), 3206 (s, C—H str. aromatic), 2217, 2163 (s, NCO str), 2975 (w, C—H str. aliphatic), 1650 (w, C=C str. aromatic), 1567 (s, C—H bend. aliphatic), 1181 (s, N—C str. aliphatic).

#### 2.2.2. $[L^2(NCO)Cu(\mu_{N,N}\text{-}NCO)]_2$, **2**

This complex was prepared by a similar method to that used for **1**, except that the ligand $L^2$ was used instead of $L^1$. The crude compound was recrystallized as blue crystals by diffusion of diethyl ether into an acetonitrile solution. The typical yield was 50% (0.353 g). *Anal.* calc. for $C_{30}H_{44}Cu_2O_4N_8$ (MW = 707.83 g·mol$^{-1}$): C, 50.91; H, 6.27; N, 15.83; found: C, 50.69; H, 6.35; N, 15.85. Selected IR data ($\nu$/cm$^{-1}$ using KBr): 3448 (m, N—H str.), 3205 (s, C—H str. aromatic), 2219, 2164 (s, NCO str), 1185 (s, N—C str. aliphatic), 2975 (w, C—H str. aliphatic), 1603 (w, C=C str. aromatic), 1389 (s, C—H bend. aliphatic), 1185 (s, N—C str. aliphatic).

### 2.3. Physical measurements

Elemental analysis (C, H and N) were obtained on a Perkin Elmer Model 2400 elemental analyzer. Infrared spectra of powdered samples in the form of KBr pellets were recorded in the range 500–4000 cm$^{-1}$ using a Bruker FT-IR spectrophotometer. Electronic absorption spectra were measured using a Braic 2100 model UV–Vis spectrophotometer with 1 cm quartz cells in the range 200–800 nm. Magnetic properties were investigated on polycrystalline samples using a Quantum Design an MPMS-XL-5 SQUID magnetometer. The magnetic susceptibility of the compounds was measured between 2 and 300 K in a constant magnetic field of 1 kOe and between −50 kOe and 50 kOe at the temperature of 2 K. All data were corrected for the temperature independent contribution of core electrons as obtained from Pascal's tables [22].

### 2.4. Single crystal structure determination

A dark-blue single crystal of **2** was used for the structure determination. The X-ray data were collected on a Bruker-Nonius X8 ApexII diffractometer equipped with a CCD area detector using