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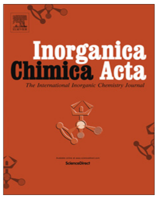

Research paper

Structural, solvatochromism and magnetic properties of two halogen bridged dinuclear copper (II) complexes: A density functional study

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Two dinuclear copper(II) complexes $[Cu(\mu\text{-}Cl)(L)Cl]_2$, **1,** $[Cu(\mu\text{-}Br)(L)Br]_2$, **2**, where L is *N,N*-dimethyl, *N′*-benzyl-ethylenediamine were synthesized and structurally characterized crystallographically and spectroscopically. Single crystal X-ray diffraction study demonstrated that in dinuclear complexes the copper(II) centers are in linked by two halo bridges. The geometry around the copper ions in **1** is square pyramidal ($\tau = 0.068$) and in **2** is an intermediate between a trigonal bipyramidal and square pyramid ($\tau = 0.498$). The magnetic coupling constants (J and zJ') of the compounds have been derived by appropriate fitting of the experimentally measured molar susceptibility variation with the temperature. The results of the measurements showed that two copper(II) centers are ferromagnetically coupled with $J = 5.0\ cm^{-1}$ for **1** and $J = 15.1\ cm^{-1}$ for **2** through halo bridges and antiferromagnetically coupled via interdimer interaction ($zJ' = -0.9\ cm^{-1}$ for **1** and $zJ' = -2.9\ cm^{-1}$ for **2**). The origin of intra- and interdimer interactions and the magnitude of the magnetic coupling have been analyzed by means of density functional theory within broken–symmetry (BS) framework. Theoretical calculations of the exchange coupling confirm the experimental results (yielding values of $J = 0.81\ cm^{-1}$ for **1** and $J = 10.51\ cm^{-1}$ for **2** and $J' = -0.1\ cm^{-1}$ for 1 and $J' = -0.56\ cm^{-1}$ for **2**). The solvatochromic property of the complexes was investigated and it was found that this phenomenon is due to structural changes of the complexes in solution.

1. Introduction

Recently numerous research works have been focused to the preparation and study of bridged binuclear copper(II) complexes with distinctive physical and/or chemical properties containing coordination chemistry [1], chromotropism [2], catalyst [3], magnetism [4], material chemistry and biology [5–8]. Different bridging ligands such as hydroxo, azido, dicyanamide, chloro, etc have been utilized, which afforded various dinuclear compounds with different topologies and magnetic properties [9–12]. Among different bridging ligands the dinuclear complexes with mono-atomic bridge ligands such as chloro ligand have received special attention due to deviation in simple magneto-structural relations [1,13–49]. This might be because of the large difference in structural features observed, along with the fact that chloride has both p and d orbitals that possibly will contribute in creating a variety of exchange pathways for the magnetic interactions [50–53]. While small changes in structure can have important effects on the magnetic properties of these systems dinuclear complexes with general formulation $LCuX_2$ (where L is bidentate ligand) have different geometries at copper center as tetrahedral [32,33], trigonal bipyramidal [34,36] and tetragonal pyramidal [37,38,40] with a number of possibilities of bond lengths and angles between the Cu(II) centers. As a result, the structural aspects impose significant effect on the magnetic properties; thus, a detailed knowledge of the magneto-structural correlation is necessary before designing magnetic materials with potential applications. Although by now a number of dichloro-bridged dinuclear complexes have been characterized magnetically and structurally [17–54] however, dibromo-bridged complexes remain too small to allow meaningful correlations. On the other hand, it has been proven that copper chelates with diamine ancillary ligand have different stabilities. The stability of 1:1 copper(II) chelate complexes is controlled by the tendency to disproportionate to 2:1 chelate and copper hydroxide. In order to avoid disproportionation reaction, the steric repulsion around the copper(II) complexes was increased by substituting a bulky alkyl group on the amine moiety of the diamine chelate ligand. It should be pointed out that several stable mono nuclear copper(II) complexes containing similar chelating ligand have been reported so

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far [55–62]. Currently, density functional theory (DFT) methods are widely used to study structural and electronic properties of coordination compounds due to their reliable results and lower computational cost in comparison with other high-level *ab initio* methods [54,63–66]. In the magneto chemistry context, the broken-symmetry formalism, originally developed by Noodleman for self-consistent field (SCF) methods [67] has been applied within the framework of density functional theory (DFT) as a practical tool to investigate magnetic interactions on rather large systems such as dinuclear, [68–73] and polynuclear, [74] complexes. Magnetic features of the complexes are compared to estimates from DFT combined with the broken-symmetry approach to gain insight into their overall magnetic behaviors. Present research work refers to the structural and magnetic properties of two dinuclear complexes of $[Cu(\mu\text{-}X)(L)X]_2$, where $X = Cl^-$ and Br^- with the aim of understanding the structural and chemical aspects that are responsible for the electronic exchange coupling through halo-bridging ligands and their potentials for magnetic interaction between the two copper centers, leading to the design of molecular magnetic materials. Moreover, the intra and intermolecular magnetic exchange coupling constant for the complexes have been calculated and the contribution of the overlap between the orbitals of two copper atoms by spin density delocalization were investigated. The obtained theoretical results are compared with experimental data and discussed to understand the relationship between structure and magnetic behavior of binuclear copper (II) complexes.

2. Experimental

2.1. General

The ligand *N,N*-dimethyl,*N′*-benzyl-ethylenediamine was prepared according to our published procedures [75]. All reagents and solvents were purchased from Merck and Aldrich and used without further purification. The solvent used in solvatochromism study were spectral-grade and purchased from commercial sources and used as received. These solvents are as follows: 1,2-dichloroethane (DCE) dichloromethane (DCM), benzonitrile (BN), acetonitrile (AN), ethanol (EtOH), methanol (MeOH), dimethylsulfoxide (DMSO), and hexamethylphosphorictriamide (HMPA).

2.2. Physical measurement

Elemental analysis (C, H, and N) were carried out at the Perkin Elmer Model 2400 elemental analyzer. The infrared spectra on powdered samples in the form of KBr pellets were recorded in range of 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 Designa MPMS-XL-5 SQUID magnetometer. Magnetic susceptibility of the compounds was measured between 2 K and 300 K in a constant magnetic field of 1 kOe and between −50 kOe and 50 kOe at temperature of 2 K. All data were corrected for temperature independent contribution of core electrons as obtained from Pascal's tables [4].

2.3. Preparation of the complexes

2.3.1. $[Cu(\mu\text{-}Cl)(L)Cl]_2$, 1

To the methanolic solution of the diamine ligand (0.178 ml, 1 mmol) was slowly added $CuCl_2{\cdot}2H_2O$ (0.170 g, 1 mmol) in methanol (10 ml) with constant stirring. A dark pale blue precipitate formed after 10 min. The mixture was stirred at room temperature for 3 h, after which the solid was filtered. Recrystallization from methanol gave blue crystals that were separated by filtration, washed with cold ether and air-dried. The yield was 50% (0.31 g). Suitable crystals for X-ray analysis were obtained after several days by the slow evaporation of solvents at room temperature. Anal. calcd. for $C_{22}H_{36}Cu_2Cl_4N_4$ (MW = 625.45 $g.mol^{-1}$): C, 42.25; H 5.80; N, 8.96; found: C, 42.07; H, 5.23; N, 8.80. Selected IR data (ν/cm^{-1} using KBr): 3445 (m, N – H str.), 3168 (s, C—H str. aromatic), 2888 (w, C—H str. aliphatic), 1685 (w, C═C str. aromatic), 1454 (s, C—H bend. aliphatic), 1009 (s, N—C str. aliphatic).

2.3.2. $[Cu(\mu\text{-}Br)(L)Br]_2$, 2

Complex **2** was prepared according to the same procedure as complex **1** using $CuBr_2$ in place of $CuCl_2{\cdot}2H_2O$. Yielded 54% as a green solid. Anal. calcd. for $C_{22}H_{36}Cu_2Br_4N_4{\cdot}H_2O$ (MW = 803.26 $g.mol^{-1}$): C, 32.17; H, 4.66; N, 6.82; found: C, 31.95; H, 4.17; N, 6.87. Selected IR data (ν/cm^{-1} using KBr): 3447 (m, N—H str.), 3163 (s, C—H str. aromatic), 2888 (w, C—H str. aliphatic), 1626 (w, C═C str. aromatic), 1455 (s, C—H bend. Aliphatic), 1008 (s, N—C str. aliphatic).

2.4. Single crystal structure determination

The X-ray data of **1** were collected with Bruker Apex-II CCD single crystal diffractometer at room temperature by using graphite-monochromated Mo-Kα radiation (λ = 0.71096) at 293.15 K and the ω-scan technique. Data were integrated using the SAINT [76] Program and subsequently used for the intensity corrections of the Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [77]. Data collections for **2** was made on STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073) at 298 K and the rotation method. Cell parameters of **2** were determined and refined using the STOE X-AREA software package [78]. A numerical absorption correction was applied using XRED [79] and X-SHAPE [80] software. The structures were solved by conventional direct methods and refined by full-matrix least square methods using F^2 data using SHELXL [81]. All non-hydrogen atoms refined as anisotropic and hydrogen atoms were placed in calculated positions. Refinement of F^2 was performed against all reflections. The weighted R-factor w*R* and goodness-of-fit S are based on F^2; conventional R-factors R are based on F, with F set to zero for negative F2. The threshold expression of $F^2 > r\ (F^2)$ is used only for calculating R-factors (gt), etc. and is not relevant to the choice of reflections for refinement. Geometrical calculations were carried out with WinGX [82] and the figures were made by the use of the Olex2 [83] programs. A summary of the crystal data and structure refinements for complexes **1** and **2** is collected in Table 1.

2.5. Computational details

We attempted estimating the exchange coupling constant by "broken-symmetry" DFT calculations [84,85] using the Gaussian09 program. The crystallographic structure of the compounds was used without optimization and simplification because the spin coupling interaction is quite sensitive to any minute change of the molecular structure. As a result, two separate calculations are carried out, one for the triplet state and another for the broken-symmetry state. The presence of a low-energy singlet (for dinuclear models) or doublet (for trinuclear models) makes it difficult to evaluate accurately the energy of the lowest singlet or doublet by a single-determinant method. To solve this problem, broken-symmetry wave functions, as proposed by Noodlemann et al., have been used [67,84]. Single-point unrestricted DFT wave functions were obtained by using the standard B3LYP hybrid functional, which is known to work very well within the BS-DFT framework in which Becke's hybrid exchange functional (B3) [86] and the cor-