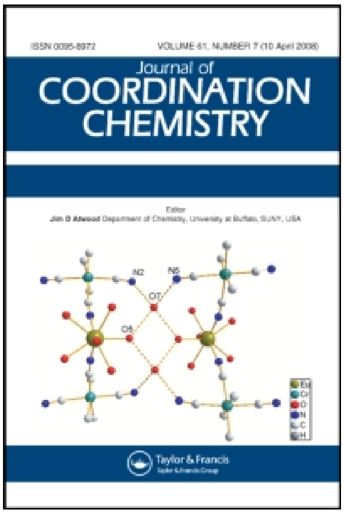

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A binuclear copper(II) complex with unusual magnetism

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A binuclear copper(II) complex $[Cu_2(\mu\text{-pyo})_2Br_4]_n$ (where pyo = pyridine N-oxide) has been synthesized and its structure determined by X-ray crystallography. This complex crystallizes in monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 11.020(3)$ Å, $b = 10.049(3)$ Å, $c = 7.905(2)$ Å, $\beta = 110.609(3)°$, and $Z = 2$. The structure was refined to final $R = 0.0311$ and $wR = 0.0721$ for 1302 observed reflections ($I > 2\sigma(I)$). In the complex, two Cu(II) ions are bridged by two pyo ligands and four bromides coordinate the Cu(II); the distance between the bridged Cu(II) ions is 3.261 Å. The variable-temperature (4–300 K) magnetic susceptibility data show that the magnetic moment is zero. Thus, there exists very strong antiferromagnetic coupling between the bridged binuclear Cu(II) ions. Density functional calculations yield a singlet-triplet splitting $2J = -1355\,cm^{-1}$.

Keywords: Magnetism; DFT calculations; Complexes

1. Introduction

Molecular magnetism has attracted considerable attention with major advances in theoretical description and application as new molecular-based materials [1–6]. In particular, special attention has been paid to the design and construction of multinuclear coordination polymers to undertake theoretical studies of their magnetic properties and develop high Tc molecular-based magnets [7–14].

In order to obtain strong magnetic coupling, judicious choice of coordinated atoms with larger electronic densities is crucial. O-donor atoms of pyrazine-1,4-dioxide possess larger electronic density than that of N-donor atom of pyrazine and lead to strong magnetic interaction in complexes of pyrazine-1,4-dioxide [15–17]. Calculations confirm that the O atom electronic densities of pyridine N-oxide and its derivatives are larger than that of N atom of pyridine and its derivatives [18]. Multi-nuclear complexes containing pyridine N-oxide and its derivatives may exhibit unusual magnetic coupling properties.

It is important to study magnetism by calculations, and multi-nuclear complexes with μ-azido [19, 20], μ-hydroxyl [21], alkoxy [21], and μ-halide [22] as bridged ligands

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have been reported. Interest in magneto-structural studies of multi-nuclear complexes resulted in synthesis, characterization, and studies of the present complex.

2. Experimental

2.1. *Materials*

All chemicals are of analytical grade and used without purification. Preparation of $[Cu_2\ (\mu\text{-pyo})_2Br_4]_n$ (pyo = pyridine), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.3565 g, 9.62×10^{-4} mol), pyridine N-oxide (0.1830 g, 1.92×10^{-3} mol) and NaBr (01980 g, 1.92×10^{-3} mol) were dissolved separately in 5 mL H_2O. The three solutions were mixed and stirred for 1 min. Deep green single crystals were obtained after the mixed solution was allowed to stand for 3 weeks at room temperature. Yield: 65%. Anal. Calcd (found) for $C_{10}H_{10}Br_4Cu_2N_2O_2$ (F_w: 636.92): C, 18.86(19.15); H, 1.58(1.76); N, 4.40(4.24); Cu, 19.95(19.93). IR(cm^{-1}): 1663 s, 1622 s, 1470 s, 1116 s, 832 s, 774 s.

2.2. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H, and N elemental analyses were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 10 KOe in the temperature range 4–300 K on a SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

2.3. *Density function calculation*

All calculations have been performed using the Amsterdam density functional (ADF) package (version 2.0.1). Vosko, Wilk, and Nusair's (VWN) functional was used for local spin density approximation (LSDA) [23]. Generalized gradient correlations have been introduced using the Bedke exchange functional [24] and the Perdew correlation functional [25]. IV basis sets in ADF containing triple-ζ basis sets and a polarization function from H to Ar were used for all atoms. The frozen core (FC) approximation for the inner core electrons was employed. The orbitals up to 2p for Cu and 1s for C, N, and O atoms were kept frozen. The scalar relativistic effect was taken into account. The convergence criterion of SCF was 10^{-6}. The numerical integration procedure applied for the calculation is the polyhedron method developed by Boerrighter *et al.* [26]. All calculations were done on an the HFRX4640 server.

2.4. *X-ray crystallographic analysis of the complex*

A single crystal of dimensions $0.20 \times 0.13 \times 0.11$ mm was selected and glued to the tip of a glass fiber. The determination of the crystal structure at 22°C was carried

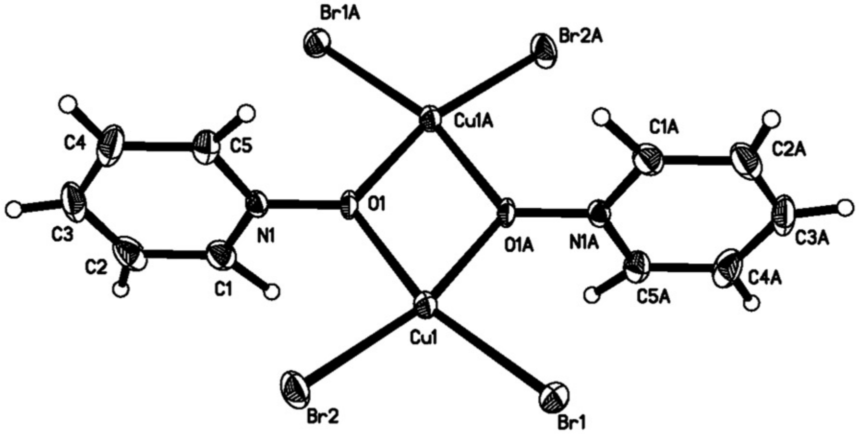

Figure 1. The coordination of the binuclear complex with the atom numbering scheme.

out on an X-ray diffractometer, Model Bruker Smart-1000 CCD, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs for structure solution and refinement were SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997), respectively. The crystal is monoclinic, space group $P2_1/c$ with $a = 11.020(3)$ Å, $b = 10.049(3)$ Å, $c = 7.905(2)$ Å, $\beta = 110.609(3)^\circ$, $V = 819.4(4)$ Å^3, empirical formula $C_{10}H_{10}Br_4Cu_2N_2O_2$, molecular weight 636.92, $D_c = 12.581$ g cm^{-3}, $F(000) = 596$, θ range 1.97–25.49°, index ranges $-13 \leq h \leq 13$, $-12 \leq k \leq 12$, $-4 \leq l \leq 9$. A total of 4253 reflections were collected and 1524 were independent ($R_{\text{int}} = 0.0363$), of which 1302 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final refinement including hydrogen atoms converged to $R = 0.0311$, $wR = 0.0721$, $(\Delta\rho)_{\max} = 0.625$ e Å^{-3}, $(\Delta\rho)_{\min} = -0.752$ e Å^{-3}. The deposition number of the crystal at the CCDC is 265,081.

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the coordination diagram for the complex with atom numbering scheme. Cu1 is coordinated by O1, O1A, Br1, and Br2, with O1 and O1A from two different pyridine N-oxides. Bond lengths and associated angles indicate that Cu1 has a distorted square coordination environment. Cu1 and Cu1A are bridged by two monodentate pyridine N-oxide bridging ligands forming a binuclear unit with a Cu $\cdots$ Cu separation of 3.261 Å; in the binuclear unit O1, O1A, Cu1, and Cu1A define a plane with no deviation.

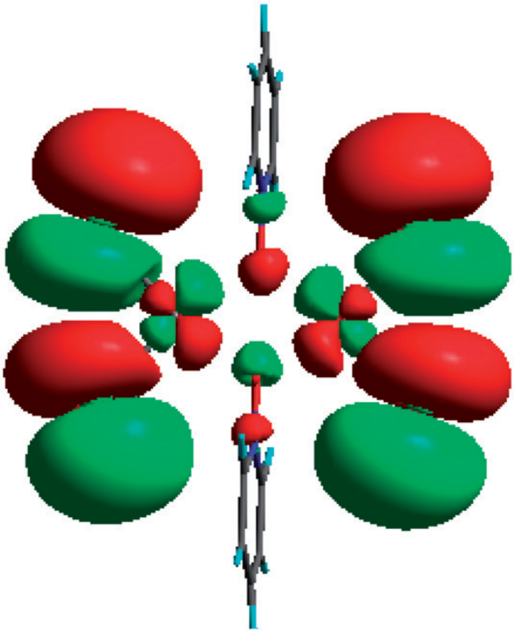

Figure 2. HOMO of the binuclear complex.

3.2. *Magnetic properties*

Data from the variable-temperature magnetic susceptibilities (4–300 K) indicate that the magnetic moment is zero from 4 to 300 K, indicating a very strong antiferromagnetic coupling between the bridged Cu(II) ions and the binuclear complex has a singlet state. In order to elucidate the magnetic mechanism and confirm the experimental result, density function calculations were performed on the binuclear complex. The calculations are based on binuclear Cu(II) Hamiltonian ($\hat{H} = -2J\hat{S}_{\mathrm{Cu}}\hat{S}_{\mathrm{Cu}}$) and Noodleman's suggestions [27, 28]. The magnetic coupling constant for a binuclear Cu(II) system can be obtained using the expression $E(\mathrm{T}) - E(\mathrm{BS}) = -2J$, where $E(\mathrm{T})$ and $E(\mathrm{BS})$ represent the energies of triplet and broken-symmetry singlet states, respectively. The energy difference value between the singlet and triplet states is calculated as $2J = -1355\,\mathrm{cm}^{-1}$. The large $2J$ will make the complex molecules to be a singlet state at room temperature, in agreement with experimental results. Ruiz has found that energy differences between the singlet and triplet states are closely related with bridging angle θ, the larger the θ, the larger the energy difference [6]. In the present complex, the θ is 109.50(11)° and is the largest bridging angle in hydroxyl- and alkoxo-bridged binuclear Cu(II) complexes [6] giving the strongest magnetic coupling.

In order to investigate the magnetic mechanism, the highest occupied molecular orbital HOMO is shown in figure 2, clearly indicating that the antiferromagnetic interaction between the pyo-bridged binuclear Cu(II) ions is due to large overlap of the Cu(II) $3d_{x^2-y^2}$ orbital with the bridging O p_y orbitals. Table 1 displays the calculated spin density distribution of some atoms for the broken-symmetry singlet state. In general, Cu(II) has one unpaired electron located in the $3d_{x^2-y^2}$ orbital.

Table 1. Calculated atoms spin population for the binuclear compound [Cu_2 (μ-pyo)$_2$$Br_4$].

Atom	Spin density	Atom	Spin density	Atom	Spin density
Cu1	−0.2994	O1	−0.007	Br1	−0.1747
Br2	−0.1787	N1	0.001	–	–
Cu1A	0.2994	O1A	0.007	Br1A	0.175
Br2	0.1746	N1A	−0.0037	–	–

However, table 1 shows that the spin population on Cu(II) is only 0.3. Also, the atoms coordinated to Cu(II) exhibit the same sign as Cu(II), suggesting significant spin delocalization for Cu(II). For O atoms of pyo bridging ligands, spin densities are very small due to two Cu(II) ions simultaneously delocalizing to the ligands, which results in very small spin density on oxygen.

In conclusion, a binuclear copper(II) complex has been synthesized with bridging pyridine N-oxide and terminal bromide, and its structure determined. Variable-temperature susceptibilities indicate that strong antiferromagnetic coupling between the bridging Cu(II) ions with magnetic moments zero from 4 to 300 K. Magnetic coupling in the complex is stronger than compared with hydroxyl and alkoxy bridging ligands. DFT calculations based on the complete binuclear structure give $2J = -1355\,\mathrm{cm}^{-1}$.

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