Dinuclear copper(II) complexes with ferromagnetic and antiferromagnetic interactions mediated by a bridging oxalato group: structures and magnetic properties of \([\text{Cu}_2\text{L}_4(\mu-\text{C}_2\text{O}_4)](\text{PF}_6)_2(\text{H}_2\text{O})_2\) and \([\text{Cu}_2\text{L}_2(\mu-\text{C}_2\text{O}_4)(\text{NO}_3)_2((\text{CH}_3)_2\text{NCOH})_2]\) \((\text{L} = \text{di-2-pyridylamine})\)

Sujittra Youngme* and Pimprapun Gnaasoot
Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
Narongsak Chaichit
Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
Chaveng Pakawatchai
Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

Received 15 April 2004; accepted 04 May 2004

Abstract

Two dinuclear Cu\textsuperscript{II} complexes of formula \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)](\text{PF}_6)_2(\text{H}_2\text{O})_2\) \((1)\) and \([\text{Cu}_2(\text{dpyam})_3(\mu-\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{DMF})_2]\) \((2)\) \((\text{dpyam} = \text{di-2-pyridylamine})\) have been synthesized and their spectroscopic and magnetic properties characterized. Complex \((1)\) crystallizes in the non-centrosymmetric monoclinic space group \(P\bar{2}_1\), while \((2)\) crystallizes in the non-centrosymmetric triclinic space group \(P1\). Compound \((1)\) involves the compressed octahedral Cu\textsuperscript{II} environment, whereas \((2)\) exhibits an elongated octahedral Cu\textsuperscript{II} geometry. Both complexes contain six-coordinate metal centers bridged by planar bis-didentate oxalate group. The geometry, spectroscopic properties and the effective magnetic moment of \((1)\) are very close to those of the recently published \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)](\text{ClO}_4)_2(\text{H}_2\text{O})_3\) and \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)][(\text{BF}_4)_2(\text{H}_2\text{O})_3]\). Thus \((1)\) is expected to exhibit a very weak ferromagnetic interaction between the Cu\textsuperscript{II} centers which is confirmed by EPR spectrum. Those of \((2)\) are comparable to those of the recently published \([\text{Cu}_2(\text{dpyam})_2(\mu-\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{DMSO})_2]\). Therefore a strong antiferromagnetic interaction is expected. The effective magnetic moment at room temperature of \((1)\) was measured to be 2.55 BM/dimer, which agrees with the spin only value of Cu\textsuperscript{II}, 2.45 BM calculated for two uncoupled spin \(= 1/2\) centers. In \((2)\) the room temperature effective magnetic moment of 2.16 BM/dimer indicates the partial spin paring by antiferromagnetic coupling. This is confirmed by the e.p.r. spectrum and is explained as a result of the magnetic interaction between the coplanar \(d_{x^2-y^2}\) orbitals on the two copper atoms.

Introduction

It is now well-known that oxalato bridges can propagate magnetic exchange interactions between paramagnetic metal ions. A number of dinuclear copper complexes with an oxalato bridge, generally formulated as \([\text{NN}]_2 \text{ or } 2\text{Cu}(\mu-\text{C}_2\text{O}_4)\text{Cu}(\text{NN})_1 \text{ or } 2\text{X}_2\), where NN is a chelating ligand, and \(X\) is a counter anion or a solvent molecule, have been structurally characterized \([1–11]\) in the past decades. The previous paper describes the crystal structure, spectroscopic properties and magneto-structural correlation of complexes \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)](\text{ClO}_4)_2(\text{H}_2\text{O})_3, [\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)][(\text{BF}_4)_2(\text{H}_2\text{O})_3]\) and \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{DMF})_2]\) \([12]\). The exchange interaction between the copper ions via the oxalate bridge is known to be strongly dependent on the geometry around the copper ions, which sensitive to nature of counter anions and terminal ligands. In order to extend the investigation by modifying to other counter ions, this paper reports the synthesis, the results of the structure determination and the magnetic properties of two new \(\mu\)-oxalato copper(II) complexes, \([\text{Cu}_2(\text{dpyam})_4(\mu-\text{C}_2\text{O}_4)](\text{PF}_6)_2(\text{H}_2\text{O})_2\) \((1)\) and \([\text{Cu}_2(\text{dpyam})_2(\mu-\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{DMSO})_2]\) \((2)\).

Experimental

Materials and physical measurements

All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were performed by the microanalytical Service...
of Science and Technological Research Equipment Center, Chulalongkorn University on Perkin-Elmer PE2400 CHNS/O Analyzer. The copper content was determined on an atomic absorption spectrophotometer.

XRD spectra were recorded with a Spectrum One Perkin-Elmer FTIR spectrophotometer as KBr pellets and, or as Nujol mulls in the 4000–450 cm⁻¹ spectral range. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer over the 8000–18,000 cm⁻¹ range. X-band powder e.p.r. spectra were obtained on a JEOL RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. The room temperature magnetic susceptibility measurements were carried out on a Faraday-type microbalance. The apparatus was calibrated with Hg[Co(NCS)₄]. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants and the temperature independent paramagnetism was estimated to be 60 × 10⁻⁶ cm³ mol⁻¹ per copper(II) ion.

**Synthesis of complexes (1) and (2)**

**Complex (1)**

**Method A.** Compound (1) was prepared by adding a solution (10 cm³) of oxalic acid (0.063 g, 0.5 mmol) to a suspension of CuCo₂(OH)₃ (0.221 g, 1.0 mmol) in H₂O (10 cm³). The mixture was added to a solution containing di-2-pyridylamine (0.342 g, 2.0 mmol) in EtOH (20 cm³) and potassium hexafluorophosphate (0.184 g, 1.0 mmol) in H₂O (10 cm³). The resulting blue solution was filtered to remove impurities. After 4 weeks, the green crystals of (1) were obtained. They were filtered, washed with mother liquor and were dried in air. Yield approximately 60%. (Found: C, 41.4; H, 3.4; Cu, 10.3; N, 13.7. C₂₄H₄₈P₂Cu₂F₁₂N₁₂O₆ calcld.: C, 41.15; H, 3.3; Cu, 10.4; N, 13.7%)  

**Method B.** Compound (1) was prepared by adding an aqueous solution (25 cm³) of CuSO₄·5H₂O (0.249 g, 1.0 mmol) to a solution of hexafluorophosphate (0.184 g, 1.0 mmol) in H₂O (20 cm³), followed by a solution of sodium oxalate (0.124 g, 1 mmol) in H₂O (10 cm³) and a solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in MeOH (20 cm³). The resulting green solution was allowed to stand at room temperature for two weeks to produce green crystals of (1). The crystals were separated by filtration and washed with the mother liquor. Yield ca. 50%. Calcld.: C₂₄H₄₈P₂Cu₂F₁₂N₁₂O₆: C, 41.15; H, 3.29; Cu, 10.37; N, 13.71%. Found: C, 41.26; H, 3.41; Cu, 10.20; N, 13.65%.

**Complex (2)**

A solution containing di-2-pyridylamine (0.342 g, 2.0 mmol) in dimethylformamide (10 cm³) was added to a solution containing Cu(NO₃)₂·3H₂O (0.482 g, 2.0 mmol) in DMF (20 cm³) and sodium oxalate (0.068 g, 0.5 mmol) in H₂O (10 cm³). Then DMF (30 cm³) was added to the resulting green solution which was filtered to remove impurities. After 4 months, green crystals of (2) were obtained, which were filtered off, washed with the mother liquor and air-dried. Yield ca. 70%. Calcld.: C₂₄H₄₈P₂Cu₂N₁₂O₁₂: C, 40.6; H, 3.9; Cu, 15.35; N, 16.92. Found: C, 40.5; H, 3.8; Cu, 15.3; N, 16.8.

Found: C, 40.5; H, 3.8; Cu, 15.3; N, 16.8 C₂₄H₄₈Cu₂. N₁₀O₁₂ calcld.: C, 40.5; H, 3.9; Cu, 15.35; N, 16.9%.

**Crystallographic data collection and structure determination of complexes (1) and (2)**

Reflection data for (1) were collected at 298 K on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at a detector distance of 4.5 cm and swing angle of -35°. A hemisphere of the reciprocal space was covered by a combination of three sets of exposures; each set had a different φ angle (0°, 88°, 180°) and each exposure of 30 S covered 0.3° in φ. Data reduction and cell refinement were performed using the program SAINT [13]. An empirical absorption correction by using the SADABS [14] program was applied, which resulted in transmission coefficients ranging from 0.5054 to 1.0000. The structure was solved by direct methods and refined by full-matrix least-squares method on Fobs with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-PC V 6.1 software package [15]. All hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. One of the hydrogen atoms of each lattice water molecule could not be located and the hexafluorophosphate groups are well ordered.

Reflection data of (2) were collected on a 4 K Bruker SMART APEX CCD area-detector diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) (at a detector distance of 6.0 cm and swing angle of -28°) using SMART program. Raw data frame integration was performed with SAINT [13], which also applied correction for Lorentz and polarization effects. Absorption corrections were applied using SADABS [14], provided an empirical absorption correction and put the standard deviations of measured intensities onto absolute scale. The structures were solved by direct methods. The software package SHELXTL V 6.12 [15] was used for structure solution and structure refinement. All non-H atoms were refined anisotropically except the nitrate-O atoms and the methyl-C atoms of DMF. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The nitrate groups are disordered with site occupancies of 0.48 and 0.52 for both conformers. Both methyl groups of the DMF ligands are also disordered with site occupancies of 0.44 and 0.56 for both conformers and some of the methyl hydrogen atoms could not be located.