The coordination chemistry of mono(di-2-pyridylamine) copper(II) complexes with monovalent and divalent oxoanions: Crystal structure and spectroscopic and magnetic properties of dinuclear $[Cu(L)(\mu\text{-}H_2PO_4)(H_2PO_4)]_2$ and polynuclear $[Cu(L)(\mu3\text{-}HPO_4)]_n$

เคมีโคออร์ดิเนชันของสารประกอบเชิงซ้อนมอนอ (ได-2-พิริดิลามีน) คอปเปอร์(II) กับออกโซแอนไอออนที่เป็นมอนอและไดเวเลนซ์: โครงสร้างผลึก สมบัติทางสเปกโทรสโกปี และสมบัติทางแม่เหล็กของไดนิวเคลียร์ $[Cu(L)(\mu\text{-}H_2PO_4)(H_2PO_4)]_2$ และพอลินิวเคลียร์ $[Cu(L)(\mu_3\text{-}HPO_4)]_n$

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Abstract

The crystal structures of two mono(dpyam)copper(II) complexes with monovalent $H_2PO_4^-$ and divalent HPO_4^{2-} oxoanions, $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4\text{-}O)]_2$ (1) and $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2) have been determined by X-ray crystallography. The dinuclear Cu(II) complex 1 was obtained by the reaction of di-2-pyridylamine (dpyam) with $Cu(NO_3)_2.3H_2O$ and KH_2PO_4 in water-ethanol solution. The molecules are linked into dinuclear units by two bridging didentate dihydrogenphosphate groups (endo/exo) in an equatorial-equatorial configuration giving a slightly distorted square pyramidal stereochemistry, $\tau = 0.12$. The Cu...Cu contact distance is unusually large (513 pm) due to the exo/endo binding of the phosphate bridges.

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Complex 2 is an example of a polymeric copper(II) derivative. Two nearest Cu(II) ions are bridged by a tridentate hydrogenphosphate group which is didentately coordinated to one copper(II) ion, and monodentately coordinated to another in an equatorial-equatorial configuration in a novel 3L, 2M coordination mode. Each copper(II) ion in 2 exhibits a tetrahedrally-distorted square-based geometry with the third oxygen atom from the hydrogenphosphate group weakly bound in an approximately axial position giving an extremely tetrahedrally distorted square-based pyramidal CuN_2O_2O' chromophore, τ= 0.12. The effective magnetic moment at room temperature of complexes 1 and 2 exhibits μ_{eff} = 2.49 and 2.09 BM, respectively, and some magneto-structural trends are discussed, along with their EPR and electronic reflectance spectra and compared with those of related complexes.

Keyword : Crystal structures; Dihydrogenphosphate complexes, Di-2-pyridylamine complexes
คำสำคัญ : โครงสร้างผลึก สารประกอบเชิงซ้อนไดไฮโดรเจนฟอสเฟต สารประกอบเชิงซ้อนได-2-พิริดิลามีน

บทคัดย่อ

ได้ศึกษาโครงสร้างผลึกของสารประกอบเชิงซ้อนของคอปเปอร์(II) ในระบบมอนอได-2-พิริดิลามีนกับออกโซแอนไอออนแบบมอนอเวเลนต์และไดเวเลนต์ คือ $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4\text{-}O)]_2$ (1) และ $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2) โดยเทคนิคเอกซเรยคริสทัลโลกราฟี สาร 1 เตรียมโดยการทำปฏิกิริยาของ ได-2-พิริดิลามีนกับคอปเปอร์(II)ไนเทรต และโพแทสเซียมไดไฮโดรเจนฟอสเฟตที่ละลายในเอทานอล โมเลกุลของสาร 1 เป็นแบบไดนิวเคลียร์โดยมีหมู่ไดไฮโดรเจนฟอสเฟตซึ่งเป็นลิแกนด์แบบไดเดนเทตทำหน้าที่เป็นสะพานลิแกนด์เชื่อมระหว่างโครมอฟอร์ของคอปเปอร์(II) ทั้งสอง จากตำแหน่ง equatorial ของโครมอฟอร์หนึ่งไปยังตำแหน่ง equatorial ของอีกโครมอฟอร์หนึ่ง (equatorial-equatorial configuration) ทำให้เกิดโครงสร้างของคอปเปอร์(II)โครมอฟอร์แบบ สแควร์พิรามิดัลที่บิดเบี้ยวเล็กน้อย (τ = 0.12) ระยะห่างระหว่างคอปเปอร์ทั้งสองยาวกว่าปกติเนื่องจากมีสะพานลิแกนด์ฟอสเฟตเชื่อมทั้งภายนอกและภายในโครงสร้างไดนิวเคลียร์

สาร 2 เป็นตัวอย่างของคอปเปอร์(II)พอลิเมอร์ โดยคอปเปอร์(II)ไอออนที่อยู่ใกล้กันเชื่อมกันโดยหมู่ไฮโดรเจนฟอสเฟตซึ่งเป็นลิแกนด์แบบไตรเดนเทต โดยมีการโคออร์ดิเนตแบบไดเดนเทตกับคอปเปอร์(II)หนึ่งไอออน และแบบมอนอเดนเทตอีกคอปเปอร์(II)ไอออน ซึ่งเชื่อมกันแบบ equatorial-equatorial โดยมีรูปแบบการโคออร์ดิเนตที่เป็นเอกลักษณ์เฉพาะตัวแบบ 3L,2M แต่ละคอปเปอร์(II)ไอออนในสาร 2 มีโครงสร้างแบบสแควร์พิรามิดัล ของ โครมอฟอร์ CuN_2O_2O' ซึ่งมีค่า τ = 0.12 จากการวัดค่าแมกเนติกโมเมนต์ที่อุณหภูมิห้องของสาร 1 และ 2 พบว่ามีค่า μ_{eff} = 2.49 ต่อไดเมอร์ และ 2.09 BM ต่อคอปเปอร์(II)ไอออน ตามลำดับ และนอกจากนี้ยังได้วิเคราะห์ถึงความสัมพันธ์ระหว่างโครงสร้างกับสมบัติทางแม่เหล็กของสาร EPR และรีเฟลคแตนท์สเปกตรา และเปรียบเทียบกับสารอื่นที่ใกล้เคียงกัน

Introduction

Reported complexes of copper(II) and didentate mono(chelating) ligand with monovalent and divalent oxoanions may be grouped in many classes for each type of oxoanions depending on the coordinating nature. Complexes with monovalent oxoanions formulated as $Cu(chelate)(OXO)_2.nH_2O$ or Cu(chelate)(OXO)(OYO).nH2O, where OXO and OYO =/ NO_2^- , NO_3^-, ClO_4^-, $CH_3CH_2COO^-$, CH_3COO^- or $HCOO^-$, so far were found to exhibit four classes of local molecular structures: [See Scheme 1] (A) monomeric tetrahedrally-distorted elongated octahedron with an extremely asymmetric didentate coordination of both oxoanions [1-7]; (B) polymeric elongated tetragonal (or rhombic) octahedron with the nearly symmetric didentate coordination of a basal oxoanion and the bridging didentate coordination in the axial positions of the second one [8-9]; (C) polymeric tetrahedrally distorted square pyramid with non-bridging monodentate and bridging didentate oxoanions [10] and (D) dinuclear tetrahedrally distorted square pyramid with non-bridging monodentate and bridging didentate oxoanions [4, 11]. While complexes with divalent oxoanions formulated as Cu(chelate)(OZO). nH_2O, where OZO = CO_3^{2-} and SO_4^{2-} involve five classes of local molecular structures: (I) monomeric distorted square-based pyramid with didentate oxoanion [12]; (II) polymeric distorted square-based pyramid with bridging tridentate oxoanion [13]; (III) monomeric square-based pyramid with monodentate oxoanion [14]; (IV) polymeric elongated octahedron with bridging didentate oxoanions [15-16]; (V) dinuclear distorted square-based pyramid with double bridges of tridentate oxoanions [17]. In order to continue exploring the coordinating and bridging natures of mono- and divalent oxoanions on these types of complexes we have now extended our studies towards tetraoxophosphate anions. So the compounds $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4)]_2$ (1) and $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2) have been synthesized, containing monovalent $H_2PO_4^-$ and divalent HPO_4^{2-} oxoanions and their structures, spectroscopic properties and magnetic behavior investigated and discussed in the context of magneto-structural correlation.

Experimental

1. Reagents and physical measurements

All reagents were commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin-Elmer PE2400 CHNS/O Analyzer by the Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University.

2. Syntheses

2.2.1 $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO4)]_2$ (1) and $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2)

An aqueous solution (30 ml) of $Cu(NO_3)_2.3H_2O$ (0.241 g, 1.0 mmol) was added to a solution of dpyam (0.171 g, 1.0 mmol) in ethanol (15 ml) and followed by an aqueous solution (20 ml) of potassium dihydrogenphosphate (0.272 g, 2.0 mmol). The resulting green solution was allowed to evaporate at room temperature. After several days, dark green crystals of $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]n$ (2) (Anal. Calc. for $C_{10}H_{10}CuN_3O_4P$: C, 36.32; H, 3.05; N, 12.71.

Found:
deposi
crystals
$(NO_3)_2$
C, 33.
H, 3.0
crystall
obtaine
characte
Greenis
$O'-H_2$
$C_{20}H_{26}$
Found:
obtaine
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Å) at a
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Found: C, 36.25; H, 2.98; N, 12.67%) were deposited. Yield ca.40%. Then green needle crystals of $[Cu_4(dpyam)_4(HPO_4)_2(NO_3)_2(H_2O)_2](NO_3)_2.2H_2O$(Anal. Calc. for $C_{40}H_{46}Cu_4N_{16}O_{24}P_2$: C, 33.13; H, 3.19; N, 15.45. Found: C, 33.20; H, 3.04; N, 15.52%) were deposited in the second crystallization. Yield ca.30%. This complex was obtained as a side product and has been recently characterized crystallographically in this laboratory. Greenish-blue crystals of $[Cu_2(dpyam)_2(\mu\text{-}O,O'\text{-}H_2PO_4)_2(H_2PO_4)_2]$ (1) (Anal. Calc. for $C_{20}H_{26}Cu_2N_6O_{16}P_4$: C, 28.05; H, 3.03; N, 9.80. Found: C, 28.14; H, 2.93; N, 9.74%) were obtained in the last crystallization. They were filtered off, washed with the mother liquid and dried in air. Yield ca.20%.

3. Crystal structure analyses

Reflection data for complexes 1 and 2 were collected at 293 K on a 1K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα 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 for 1 and 35 s for 2, covered 0.3° in ω. Data reduction and cell refinements were performed using the program SAINT [18]. An empirical absorption correction by using the SADABS [19] program was applied, which resulted in transmission coefficients ranging from 0.790 to 1.000 for 1 and 0.854 to 1.000 for 2. The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{obs})^2$ with anisotropic thermal parameters for all nonhydrogen atoms using the SHELXTL-PC V 5.03 [20] software package. All hydrogen atoms in 1 and 2 were located by difference synthesis and refined isotropically. The molecular graphics were created by using SHELXTL-PC. Figs. 1 and 2 illustrate the structures of complexes 1 and 2, respectively, and the atom numbering scheme used.

4. Physical measurements

IR spectra were recorded on a Spectrum One Perkin-Elmer FT-IR spectrophotometer as KBr pellets in the 4000-450 cm^{-1} spectral range. Diffuse reflectance measurements from 9090 to 20 000 cm-1 were recorded as polycrystalline samples using a Perkin-Elmer Lambda 2S spectrophotometer equipped with an intergrating sphere attachment. Barium sulfate was used as the reflectance standard. X-band powder EPR spectra were recorded on a JEOL RE2X electron spin resonance spectrometer. The effective magnetic moment measurements at room temperature were using a Faradays type microbalance. 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 $60x10^{-6}$ cm^3 mol^{-1} per Cu(II) ion.

Results and discussion

1. Description of the crystal structure

1.1 $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4)]_2$ (1)

The structure of 1, Fig. 1, is a centrosymmetric dimer consisting of two $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4)]$ units being doubly bridged by two didentate dihydrogenphosphato ligands. The local molecular structure of the copper atom involves a square pyramidal CuN_2O_2O' chromophore.

The basal plane consists of two oxygen atoms of the two bridging dihydrogenphosphato groups, O(5) and O(8A) and of dpyam ligand coordinated through two nitrogen atoms. The dpyam ligand bonds in the plane, almost symmetrically, with Cu-N distances of 1.991(1) and 1.997(1) Å and a bite angle of 88.1(1)°. The equatorial Cu(1)-O(8A) and Cu(1)-O(5) bond distances are slightly shorter with values of 1.964(1) and 1.987(1) Å. The fifth axial coordination site is occupied by one oxygen atom of non-bridging monodentate dihydrogenphosphato group at the Cu-O distance of 2.271(1) Å. The four in-plane atoms, N(1), N(2), O(5) and O(8A) are essentially planar, r.m.s. deviation 0.0598 Å with a slightly tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes = 14.0°). The Cu atom lies above this plane, 0.16 Å toward O(1). The copper chromophore can be described as having a slightly distorted square pyramidal geometry. The tetragonality, T = 0.874 based on the changes in bond lengths (T = the mean in-plane bond length/ the mean out-of-plane bond length). The τ-value defined to describe the degree of trigonal distortion is 0.12 $\{\tau = (\alpha_1-\alpha_2)/60\}$ where α_1 = O(5)-Cu(1)-N(1) and α_2 = O(8A)-Cu(1)-N(2). As the regular trigonal bipyramid and square-based pyramid have τ values of 1.00 and 0.00, respectively, the stereochemistry of the CuN_2O_2O' chromophore of 1 is best described as square-based pyramidal, with a slight trigonal distortion. The Cu...Cu distance is 5.136(2) Å.

The O(8)-P(2)-O(5) bridging angle of 115.7(1)° is greater than 109.5(of the ideal tetrahedral geometry, and the remaining angles involve less deviation from 109.5° [O(5)-P(2)-O(7) 105.9(1), O(5)-P(2)-O(6) 105.6(1), O(7)-P(2)-O(6) 106.8(1) and O(8)-P(2)-O(6) 112.6(1)°]. The coordinated P-O bonds, 1.518(1) and 1.506(1) Å, are shorter than the uncoordinated P-OH bonds, 1.564(1) and 1.559(1) Å. These are normally found for the two-coordinate bridging coordination of the dihydrogenphosphate anion. The non-bridging monodentate dihydrogenphosphato group involves O-P-O angles ranging from 104.1(1) to 115.1(1)°. The P-OH bonds, 1.558(1) and 1.581(1) Å, are longer than the P-O bonds, 1.512(1) and 1.519(1) Å, which is in usual observation. The uncoordinated P-O bond distance, 1.519(1) Å, is slightly longer than the coordinated one, 1.511(1) which is unusual. This arises due to the hydrogen bond involved to the uncoordinated P-O bond. The P-O distances in both the monodentate dihydrogenphosphato group and the dihydrogenphosphato bridge are ranging from 1.506(1) to 1.519(1) Å, while the P-OH bond distances vary from 1.558(1) to 1.581(1) Å. This is consistent with the general observation that P-OH bonds are longer than P-O bonds in primary and secondary phosphates.

The lattice structures are stabilized by strong to weak hydrogen bonding network between the amine N and non-bridged monodentate dihydrogenphosphate oxygen atoms with a distance of 2.359 Å. Other hydrogen bondings occur between the oxygen atoms of the monodentate dihydrogenphosphate groups (distance 2.582 Å) and between the oxygen atoms of the monodentate dihydrogenphosphate and the oxygen atoms of the bridging didentate dihydrogenphosphate (distances 2.631- 2.648 Å).

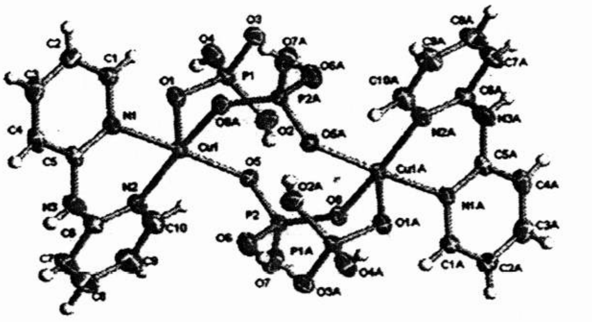


Figure 1. ORTEP 50% probability plot of $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4)]_2$ (1) Atoms with an "A" are generated by an inversion centre.

1.2 $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2)

The structure of 2, Fig. 2 consists of a neutral and polymeric infinite chain structure of $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]$ unit being bridged by tridentate hydrogenphosphato ligand. The local molecular structure of the copper atom involves square pyramidal CuN_2O_2O' chromophore in an equatorial-equatorial configuration. The basal plane consists of two oxygen atoms from two equivalent bridging hydrogenphosphato groups and of dpyam ligand coordinated through two nitrogen atoms. The dpyam ligand bonds in the plane, almost symmetrically, with Cu-N distances of 1.969(1) and 1.994(1) Å, and a bite angle of 92.0(6)°. The equatorial Cu(1)-O(1) and Cu(1)-O(4) bond distances are slightly shorter with values of 1.946(1) and 1.919(1) Å. The third oxygen atom from hydrogenphosphate group is bent towards the Cu atom to complete a fifth coordination site in an axial position at a longer distance of 2.719(2) Å which is markedly more than other atom coordinate, giving the distorted square-based pyramidal stereochemistry. The four in-plane atoms, N(1), N(2), O(1) and O(4) are not planar, r.m.s. deviation 0.562 Å with a marked tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes = 45.56°). The Cu atom lies above this plane, 0.202 Å toward O(2A). The copper chromophore can be described as having an extremely tetrahedrally distorted square pyramidal geometry with the tetragonality, T of 0.720 and τ-value of 0.12. The Cu...Cu distance is 5.955(2) Å.

The hydrogenphosphato group in this compound involve a highly unusual tridentate 3L, 2M coordination mode: didentately coordinated to one copper chromophore and monodentately bonded to another. To the best of our knowledge this coordination mode of the bridging hydrogenphosphate present in complex 2 is unique for the transition metal complexes.

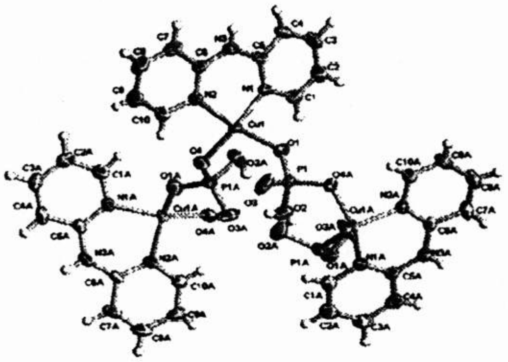


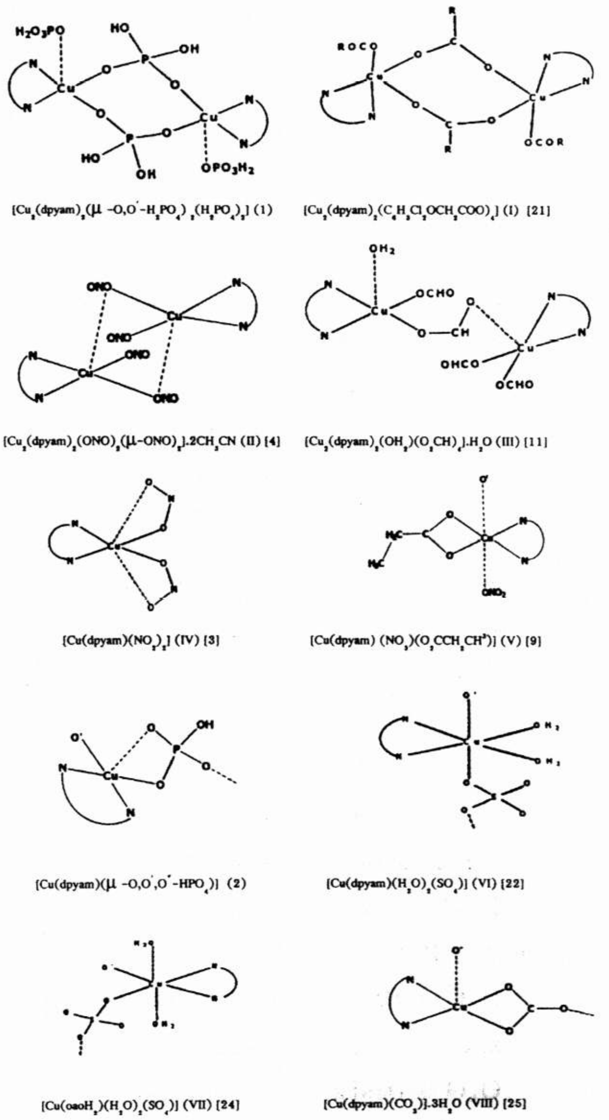
Figure 2. ORTEP 50% probability plot of the cation in $[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]_n$ (2)

The coordinated P-O bonds, 1.519(1), 1.510(2) and 1.531(1) ?, are shorter than the uncoordinated P-OH bond, 1.588(2) ?. This is usually found for the three-coordinate bridging coordination of the hydrogenphosphate anion. The tridentate hydrogenphosphato group involves

O-P-O angles ranging from 101.9(1) to 111.7(1)°. The lattice structure is stabilized by a hydrogen-bonding network between the amine N and an oxygen atom of the hydrogenphosphate groups with a short contact distance of 2.662 Å; between carbon atom of pyridine ring and an oxygen atom of the hydrogenphosphate groups with a contact distance of 2.874 Å.

2. Structural comparison

The square pyramidal CuN_2O_2O' chromophore of 1 corresponds to the square pyramidal CuN_2O_2O' chromophore observed from the copper environments of the known dinuclear structures; $[Cu_2(dpyam)_2(C_6H_3Cl_2OCH_2COO)_4]$ (I) [21], $[Cu_2(dpyam)_2(ONO\text{-}O,O')_2(\mu\text{-}ONO\text{-}O)_2].2CH_3CN$ (II) [4] and $[Cu_2(dpyam)_2(OH_2)(O_2CH)_4].H_2O$ (III) [11] (Table 1 and Scheme I). The structure of 1 and I, involve the two-coordinate bridging coordination of oxoanions in equatorial-equatorial and axial-equatorial configurations, respectively. Additionally, there are some differences in the five-coordinate distortion with the trigonality $\tau = 0.12$ for 1 and $\tau = 0.48$ for I, along with the tetragonality $T = 0.874$ and 0.897 for 1 and I, respectively. The stereochemistry of the CuN_2O_2O' chromophore of 1 is best described as square-based pyramidal with a slight trigonal distortion, while that of I can be described as having an intermediate geometry between regular square pyramid and trigonal bipyramid. The nitrite groups in II act as two non-bridging monodentate anions and two bridging monodentate anions while the formate groups in III act as three non-bridging monodentate anions and a single bridging didentate anion. The bridging oxoanion ligands of II and III joined copper atoms in an axial-equatorial configuration which is markedly different from the equatorial-equatorial configuration in 1. These dinuclear complexes are structurally different from monomeric and polymeric complexes, Table 1. The coordination around the copper atoms of monomeric complexes involves the tetrahedrally distorted elongated tetragonal-octahedral geometry with the long off-the-z-axis coordination of the second oxygen atoms from each OXO^- ligand in the axial positions (Scheme I, IV). While an important feature of the structures of polymeric complexes is the two-coordinate bridging coordination of the oxoanion, which involve an unsymmetrical bonding to the Cu atom in the elongated rhombic octahedral configuration (Scheme I, V). The polymeric structure of 2 is comparable to those of complexes with divalent sulfate anion $[Cu(dpyam)(H_2O)_2(SO_4)]$ (VI) [22], $[Cu(en)(H_2O)_2(SO_4)]$ [15], $[Cu(bpy)(H_2O)_2(SO_4)]$ [16], $[Cu(phen)(H_2O)_2(SO_4)]$ [23], and $[Cu(oaoH_2)(H_2O)_2(SO_4)]$ (VII) [24] all of which involve polymeric chain structures with bridging didentate sulfate groups and coordinated water and very comparable to that of the complex with divalent carbonate group $[Cu(dpyam)(CO_3)].3H_2O$ (VIII) [25] (Table 2 and Scheme I) which involves polymeric square pyramidal structure with bridging tridentate carbonate group and similar chromophore geometry. The bridging carbonate ligand joined copper atoms in an axial-equatorial configuration, while in 2 the bridging HPO_4^{2-} oxoanion joined copper atoms in an equatorial-equatorial configuration. However, they differ from the square pyramidal monomeric complexes, $[Cu(tmen)(H_2O)_2(SO_4)].H_2O$ [14], $[Cu(dpyam)(CO_3)(H_2O)].2H_2O$ [12] which involve the monodentate sulfate and didentate carbonate anion, respectively, and dinuclear complexes $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (IX) [24] and $[Cu(dpyam)(CO_3)]_2(H_2O)$ (X) [17]. which involve the square pyramidal structures with bridging didentate sulfate and carbonate groups (Scheme I). The bridging sulfate and carbonate ligands joined copper atoms in an axial-equatorial configuration. In comparison to the copper(II) complexes with divalent oxoanion, the carbonate and sulfate anions exhibit the marked difference both in the nature of coordinating and bridging modes, resulting in different local molecular geometries



$[Cu_2(dpyam)_2(\mu\text{-}O,O'\text{-}H_2PO_4)_2(H_2PO_4)_2]$ (1)

$[Cu_2(dpyam)_2(C_6H_3Cl_2OCH_2COO)_4]$ (I) [21]

$[Cu_2(dpyam)_2(ONO)_2(\mu\text{-}ONO)_2].2CH_3CN$ (II) [4]

$[Cu_2(dpyam)_2(OH_2)(O_2CH)_4].H_2O$ (III) [11]

$[Cu(dpyam)(NO_2)_2]$ (IV) [3]

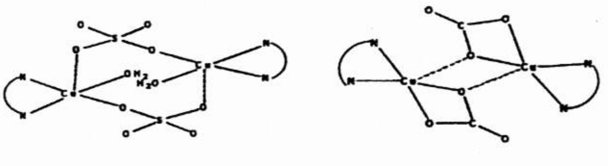
$[Cu(dpyam)(NO_3)(O_2CCH_2CH^3)]$ (V) [9]

$[Cu(dpyam)(\mu\text{-}O,O',O''\text{-}HPO_4)]$ (2)

$[Cu(dpyam)(H_2O)_2(SO_4)]$ (VI) [22]

$[Cu(oaoH_2)(H_2O)_2(SO_4)]$ (VII) [24]

$[Cu(dpyam)(CO_3)].3H_2O$ (VIII) [25]



$Cu_2(oaoH_2)_2(H_2O)_2(SO_4)_2]$ (IX) [24]

$[Cu_2(dpyam)_2(CO_3)_2].H_2O$ (X) [17]

Scheme I. Representation of the coordination modes described to date for the mono(chelate) copper(II) complexes with monovalent and divalent oxoanions.

3. ESR spectra and magnetic properties

The polycrystalline ESR spectrum of 1 at both room temperature and liquid nitrogen temperature (77 K) are axial, $g_{//} = 2.270$ and $g_{\perp} = 2.027$ at room temperature, with decreasing temperature to 77 K, $g_{//} = 2.273$ and $g_{\perp} = 2.022$, consistent with the $d_{x^2-y^2}$ ground state of a square pyramidal CuN_2O_2O' chromophore present ($g_{//} >> g_{\perp} > 2.0$). In 2 at room temperature the spectra is isotropic type with $g_i = 2.127$ giving no information regarding to the electronic ground state, While at liquid nitrogen temperature the ESR spectrum is axial with $g_{//} = 2.291$ and $g_{\perp} = 2.003$, consistent with the $d_{x^2-y^2}$ ground state of a tetrahedrally distorted square-based pyramidal CuN_2O_2O' chromophore present ($g_{//} > g_{\perp} > 2.0$). For all complexes, the triplet signal is not observed at both temperatures, hence no information regarding the magnetic interaction between two copper(II) centers is given from EPR spectrum.

The effective magnetic moment at room temperature of complexes 1 and 2 (μ_{eff}, 2.49 and 2.09 BM, respectively) are close to the normal value (2.45 BM) for the uncouple copper(II) complexes suggesting noninteracting between the copper(II) centres at room temperature. As the complexes 1 and 2 involve the square pyramidal geometry with an unpaired electron in $d_{x^2-y^2}$ orbital and $H_nPO_4^{(3-n)-}$ bridges join copper atoms in an equatorial-equatorial configuration, a substantial coupling is probably occurring through Cu-O-P-O-Cu.

4. Electronic and IR spectra

The electronic diffuse reflectance spectrum of 1 shows a broad band at 14.88 kK. This observed single broad peak is consistent with the square pyramidal stereochemistry and assigned to be d_{z^2}, d_{xy}, d_{xz}, d_{yz} $\rightarrow$ $d_{x^2-y^2}$ transition. Complex 2 exhibits a main peak at 14.4 kK with a shoulder at 11.2 kK. The transitions may be assigned as the d_{xy}, d_{z^2} $\rightarrow$ $d_{x^2-y^2}$ transition for the low-energy peak and the d_{xz}, d_{yz} $\rightarrow$ $d_{x^2-y^2}$ transition for the high-energy peak.

The infrared spectrum of 1 shows bands at ca.1353; 1330, 1112 and 1049; 975 and 881; and a broad band ca. 522-488 cm^{-1} characteristic of P-O-H in-plane deformation, ν(P-O), ν(P-O-(H)) and δ(O-P-O), respectively, which corresponds to those of others dihydrogenphosphate complexes. That of 2 shows two strong and one medium bands at 1092, 1056 and 968 cm^{-1}, characteristic of a ν(P-O), and δ(O-P-O) peaks are found at 585 and 555 cm^{-1} of hydrogenphosphate anions [27].

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References

1. Procter, I.M., Hathaway, B.J., and Hodgson, P.G. 1972. The electronic properties and stereochemistry of the copper(II) ion-VIII : Mono(ethylenediamine)-and mono (2,2′-bipyridyl)-copper(II) complexes. **Inorg. Nucl. Chem.** 34: 3689-3697.
2. Youngme S., Pakawatchai, C. Fun, H.K. and Chinnakali, K. 1998. **Acta Crystallogr., Sect. C** 54: 1586.
3. Youngme, S., Tonpho, S., Chinnakali, K., Chantrapromma, S., and Fun, H.K. 1999. Synthesis, spectroscopic characterisation and X-ray crystal structures of acetato (di-2-pyridylamine) nitritocopper(II) monohydrate and (di-2-pyridylamine) dinitritocopper(II). **Polyhedron.** 18: 851-856.
4. Camus, A., Marsich, N., Lanfredi, A.M.M., Ugozzoli, F., and Massera, C. 2000. Copper(II)nitrito complexes with 2,2′-dipyridylamine. Crystal structures of the [(acetato)(2,2′-dipyridylamine) (nitrito-O,O′)copper(II)] and [(2,2′-dipyridylamine)(nitrito-O,O′)(μ-nitrito-O)copper(II)]$_2$2(acetonitrile), **Inorg. Chim. Acta** 309: 1-9.
5. Youngme, S., Chaichit, N., and Damnatara, K. 2002. The coordination chemistry of dinitrato-di-2-pyridylamine copper(II). Crystal structures of *catena*-poly[[(di-2-pyridylamine)(nitrato-O,Ő)copper(II)]-μ-nitrato-O:O′] and bis(nitrato-O,O′) (di-2-pyridylamine)copper(II) dihydrate. **Polyhedron**. 21: 943-950.
6. Stibrany, R.T., Potenza, J.A., and Schugar. H.J. 1996. Synthesis, structure, and spectroscopic properties of (nitrito-O,O′)[tris[2-(1-methyl)imidazolyl] methoxymethane]copper(II),Cu(II)

$(TIMM)(NO_2)_2^1$. **Inorg. Chim. Acta.** 243: 33-37.

7. Bhalla, R., Helliwell, M., and Garner, C.D. 1997. Synthesis and Coordination Chemistry of the Bis(imidazole) Ligand, Bis(1-methyl-4,5-diphenylimidaz-2-oyl)(benzyloxy) methane. **Inorg. Chem.** 36: 2944-2949.
8. Ray, N., Tyagi, S., and Hathaway, B.J. 1982. **Acta Crystallogr.**, Sect. B 38: 1574.
9. Youngme, S., Pakawatchai, C, and Fun,. H.K. 1998. **Acta Crystallogr.**, Sect. C 54: 451.
10. Coombs, T.D., Brisdon, B.J., Curtis, C. P., Mahon, M.F., Brewer, S.A., and Willis, C.R. 2001. Syntheses and crystal structures of Cu(II) and Zn(II) complexes of 2,2′-dipyridyl (N-propenyl)amine. **Polyhrdron** 20: 2935-2943.
11. Youngme, S., Somjitsripunya, W., Chinnakali, K., Chantrapromma, S., and Fun, H.K. 1999. The crystal and molecular structures of dĩhydroxy-bis(di-2-pyridylamine) dinitratodicopper(II) and aqua-μ-formato-triformato-bis(di-2-pyridylamine) dicopper(II) monohydrate. Polyhedron. 18: 857-862.
12. Akhter, P., Fitzsimons, P., and Hathaway, B. 1991. **Acta Crystallogr.**, Sect. C 47:308.
13. Sletten, J., 1984. **Acta Chem. Scand.**, Sect. A 38: 491.
14. Balvich, J., Fivizzani, K.P., Pavkovic, S.F., and Brown, J.N. 1976. Preparation, properties, and crystal and molecular structure of diaquosulfato (N,N,N′N′-tetramethylethylenediamine)copper(II) hydrate. **Inorg. Chem.** 15: 71-74.
15. Dunai-Jurio, M., and Porai-Koshits, M.A. 1966. **Chem. Zvesti** 20: 783.
16. Tedenac, J.C., Phung, N.D., Avinens, C., and Maurin, M. 1976. Stereochimie du motif de coordination dans les complexes a ligands mixtes du type $MII(bipy)(H_2O)_2AB_4$ (M^{II} = Ni^{II} ou Cu^{II}; AB_4^{2-} = SO_4^{2-} ou BeF_4^{2-}) bipy: 2,2′ bipyridine. **Inorg. Nucl. Chem.** 38: 85-89.
17. Youngme, S., Chaichit, N., Kongsaeree, P., Albada, G.A. van, and Reedijk, J. 2001. Synthesis, structure, spectroscopy, and magnetism of two new dinuclear carbonato-bridged Cu(II) complexes. **Inorg. Chim.** Acta. 20: 232-240.
18. Siemens. SAINT. 1996, Version4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA.1996.
19. Sheldrick, G.M. 1996. SADABS, Program for Empirical Absorption correction of Area Dectector Data, University of Göttingen, Göttingen, Germany.
20. Siemens. SHELXTL. 1996, Version 5 Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA. 1996.
21. Psomas, G., Raptopoulou, C.P., Iordanidis, L., Dendrinou-Samara, C., Tangoulis, V., and Kessissoglou. D.P. 2000. Structurally Diverse Copper(II)-Carboxylato Complexes: Neutral and Ionic Mononuclear Structures and a Novel Binuclear Structure. **Inorg. Chem.** 39: 3042-3048.
22. Youngme, S., Chaichit, N., Pakawatchai, C., and Booncoon, S. 2002. The coordination chemistry of mono and bis(di-2-pyridylamine)copper(II) complexes: preparation, characterization and crystal structures of $[Cu(L)(NO_2)_2]$, $[Cu(L)(H_2O)_2(SO_4)]$, $[Cu(L)_2(NCS)](SCN)\cdot0.5DMSO$ and $[Cu(L)_2(SCN)_2]$. **Polyhedron.** 21: 1279-1288.
23. Xu, L., Wang, E., Peng, J., and Huang, R. 2003. A novel coordination polymer with

double chains structure: hydrothermal syntheses, structures and magnetic properties of $[Cu(phen)(H_2O)_2SO_4]_n$ (phen=1,10-phenanthroline). Inorg. Chem. Comm. 6: 740-743.

24. Endres, H., Noethe. D., Rossato, E., and Hatfield, W.E. 1984. Monomeric and anion-bridged dimeric and polymeric oxamide oxime complexes of copper(II): preparation, crystal and molecular structures, and magnetic properties. Inorg. Chem. 23: 3467-3473.

25. Sletten J., 1984. Acta Chem. Scand. A 38: 491.

26. Roca, M., Amoros, P., Cano, J., Marcos, M.D., Alamo, J., Beltran-Porter, A., and Beltran-Porter, D. 1998. Prediction of Magnetic Properties in Oxovanadium(IV) Phosphates: The Role of the Bridging PO_4 Anions. **Inorg. Chem.** 37: 3167-3174.

27. Zhang, Y., Huashalter, R.C., and Zubieta, J. 1997. Hydrothermal synthesis and crystal and molecular structure of a binuclear dioxovanadium(V) species exhibiting a bridging HPO_4^{2-} ligand, $[(VO_2)_2(HPO_4)$ (2,2′-bipy)2]·H_2O. **Inorg. Chim. Acta.** 260: 105-110.

Table 1 Structural data and electronic spectra of **1** and some relevant complexes

Complex	Coordination geometry	τ	Chromophore	Tetragonality	Tetrahedral twist, °	Bridging configuration	J value (cm^{-1})	Electronic spectra (kK)	ESR spectrum (r.t)	References
Dinuclear $[Cu(dpyam)(\mu\text{-}O,O'\text{-}H_2PO_4)(H_2PO_4)]_2$ (1)	dinuclear SP	0.120	CuN_2O_3	0.874	14.00	equatorial-equatorial	-	14.88	$g_{//}=2.270$ $g_{\perp}=2.027$	this work
$[Cu(dpyam)(C_6H_3Cl_2OCH_2COO)_2]_2$ (I)	dinuclear dist.SP	0.480	CuN_2O_3	0.897	-	axial-equatorial	-0.8	-	-	21
$[Cu(dpyam)(ONO\text{-}O,O)(\mu\text{-}ONO\text{-}O)]_2.2CH_3CN$ (II)	dinuclear dist.SP	0.000	CuN_2O_3	0.813	-	axial-equatorial	-	-	-	4
$[Cu_2(dpyam)_2(O_2CH)_4(OH_2)].H_2O$ (III)	dinuclear dist.SP	0.113, 0.096	CuN_2O_3	0.841	16.01, 19.35	axial-equatorial	-	15.67	-	11
Monomeric $[Cu(dpyam)(NO_2)_2]$ (IV)	monomeric dist.oct.	0.020	$CuN_2O_2O_2'$	0.813	31.16	-	-	13.89, (14.00)	$g_i=2.117$	3
$[Cu(dpyam)(O_2CCH_3)_2].2H_2O$	monomeric dist.oct.	-	$CuN_2O_2O_2'$	0.764	34.38	-	-	13.80	$g_{//}=2.230$ $g_{\perp}=2.016$	2
$[Cu(TIMM)(NO_2)_2]$	monomeric dist.Oct	-	$CuN_2O_2O_2'$	0.792	-	-	-	15.2	$g_{//}=2.218$ $g_{\perp}=2.026$	6
$[Cu(BimOBz)(NO_3)_2]$	monomeric dist.Oct	-	$CuN_2O_2O_2'$	0.779	15.6	-	-	-	$g_{//}=2.280$ $g_{\perp}=2.060$	7
Polymeric $[Cu(dpyam)(NO_3)_2]$	polymeric elong.oct.	-	$CuN_2O_2O_2'$	0.824, 0.817	7.00, 3.80	-	-	14.34(~10.85sh)	$g_{//}=2.307$ $g_{\perp}=2.074$	5
$[Cu(dpyam)(NO_3)(O_2CCH_2CH_3)]$(V)	polymeric elong.oct.	-	$CuN_2O_2O_2'$	0.753	-	axial-equatorial	-	14.79(~10.00sh)	$g_i=2.062$	9
$[Cu(dpyam)(O_2CCH_3)(O_2ClO_2)]..H_2O$	polymeric elong.oct.	-	$CuN_2O_2O_2'$	0.765	-	axial-axial	-	14.85 (~10.80sh), 15.80(~10.00sh)	$g_{//}=2.250$, $g_{\perp}=2.062$ $g_1=2.053$, $g_2=2.065$ $g_3=2.273$	8

dpyam = di-2-pyridylamine; bpy = 2,2′-bipyridine; TIMM = Tris[2-(1-methyl)imidazolyl]methoxymethane; BimOBz = bis(1-methyl-4,5-diphenylimidaz-2-oyl)(benzyloxy) methane; dist.oct= distorted octahedral; dist.SP = distorted square pyramidal; elong.oct. = elongated octahedral.

Table 2 Structural data and electronic spectra of 2 and some relevant complexes

Complex	Coordination geometry	τ	Chromophore	Tetragonality	Tetrahedral twist,°	Configuration	J value (cm^{-1})	Electronic spectra (kK)	ESR spectrum (r.t)	References
Polymer [Cu(dpyam)(HPO_4)] (2)	polymeric dist. SP	0.120	CuN_2O_3	0.720	45.5	equatorial-equatorial	-	14.40(~11.20sh)	$g_{//}$=2.270 $g_\perp$=2.027	This work
Cu(dpyam)(CO_3)].3H_2O (VI)	polymeric dist. SP	0.003	$CuN_2O_2O_2'$	0.861	-	axial-equatorial	-	15.60	-	25
[Cu(dpyam)(H_2O)$_2$(SO_4)] (VII)	polymeric elong.oct	-	$CuN_2O_2O_2'$	0.815	15.8	axial-axial	-	13.70 (~110.26sh)	-	22
[Cu(phen)(H_2O)$_2$(SO_4)]	polymeric elong.oct	-	$CuN_2O_2O_2'$	0.808	-	axial-axial	-3.8	-	-	23
[Cu(oaoH$_2$)(H_2O)$_2$(SO_4)] (VIII)	polymeric dist.oct	-	$CuN_2O_2O_2'$	0.832	-	equatorial-equatorial	-1.0	-	g_i=2.155	24
Monomer [Cu(dpyam)(CO_3)(H_2O)]. 2H_2O	monomeric dist.SP	0.096	CuN_2O_3	0.899	50.3	-	-	15.00 (~11.50sh),	-	12
[Cu(tmen)(H_2O)$_2$(SO_4)].H_2O	monomeric dist.SP	0.085	CuN_2O_3	0.908	-	-	-	-	-	14
Dimer [Cu(oaoH$_2$)(H_2O)(SO_4)]$_2$(IX)	dinuclear dist.TP	0.145	CuN_2O_3	0.774	-	axial-equatorial	-1.27	-	$g_{//}$=2.291 $g_\perp$=2.073	24
[Cu(dpyam)(CO_3)]$_2$.H_2O (X)	dinuclear dist.SP	0.220	CuN_2O_3	0.815	5.9^a, 5.1^b	axial-equatorial	-9.9	15.75	$g_{//}$=2.230 $g_\perp$=2.080	17

dpyam = di-2-pyridylamine; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroine; oaoH$_2$; oxamide oxime; tmen = N,N,N′,N′-tetramethylethylenediamine; ^{a}chromophore A ; ^{b} chromophore B; dist.oct = distorted octahedral; dist.SP = distorted square pyramidal; dist.TP = distorted tetragonal pyramidal