1726 *Inorg. Chem.* **2001,** *40,* 1726−1727

Structure and Magnetic Properties of a Pyrophosphate-Bridged Cu(II) Complex

Paul E. Kruger,*,† Robert P. Doyle,† Miguel Julve,*,‡ Francesc Lloret,‡ and Mark Nieuwenhuyzen§

Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland, Department de Química Inorgànica, Facultat de Química, Universitat de València, Dr. Moliner 50, E-46100 Burjassot, València, Spain, and the Chemistry Department, Queen's University, Belfast, U.K. BT9 5AG

Received July 14, 2000

Considerable current interest revolves around the chemistry and biochemistry associated with polyphosphate anions because they are ubiquitous in biology. They participate in a diverse series of bioenergetic processes ranging from oxidative phosphorylation including ATP (adenosine 5′-triphosphate) production,[1] through nucleic acid mediated information processing, to energy storage and transduction.[2] A pivotal intermediate within this family is pyrophosphate, $P_2O_7^{4-}$. It is somewhat surprising then that its coordination chemistry remains practically unexplored as metal ions are heavily involved in phosphate metabolism.[3] This relative dearth may be a consequence of its ready hydrolysis as exemplified by those bioinorganic reactions catalyzed by the inorganic pyrophosphatases.[4] As far as we are aware, the molecular structures of only two coordination compounds containing bridging pyrophosphate have been reported, namely, $[(CuL)_4P_2O_7]\cdot nH_2O$ (HL = 2-formylpyridinethiosemicarbazone; $n = 9-12$)[5] and $(C_8H_{11}NH)_4[(VO)_4(P_2O_7)_2(OCH_3)_4]$.[6]

We have begun a study of pyrophosphate-bridged coordination compounds to investigate its ability to mediate electronic interactions between paramagnetic metal centers. We present here our initial magnetostructural investigations concerning the novel compounds $\{[(bipy)Cu(H_2O)]_2(\mu\text{-}P_2O_7)\cdot 7H_2O\}$ (**1**) and its related dehydrated products $\{[(bipy)Cu(H_2O)]_2(\mu\text{-}P_2O_7)\}$ (**2**) and $\{[(bipy)Cu]_2(\mu\text{-}P_2O_7)\}$ (**3**).

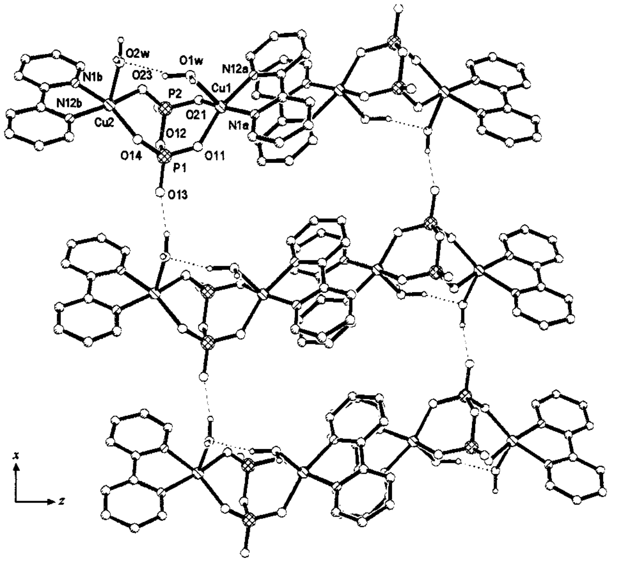

Figure 1. Packing diagram of complex **1** showing the 3-D intermolecular H-bonding and $\pi-\pi$ interactions; waters of crystallization have been omitted for clarity.

Compound **1** is obtained in good yield (ca. 90%) as sky blue parallelepipeds by slow evaporation of concentrated aqueous solutions containing stoichiometric amounts of $Cu(NO_3)_2\cdot 3H_2O$, 2,2′-bipyridine, and $Na_4P_2O_7\cdot 4H_2O$. The structure[7] of **1** consists of neutral $\{[(bipy)Cu(H_2O)]_2(\mu\text{-}P_2O_7)\}$ dinuclear copper(II) units and seven waters of crystallization linked by an extensive network of hydrogen bonding, Figure 1. The geometry of the copper atoms is distorted square pyramidal with two bipy nitrogens and two pyrophosphate oxygen atoms building the basal plane. They are shifted by 0.226 [Cu(1)] and 0.190 Å [Cu(2)] from the mean basal plane toward the axially coordinated water molecules O(1w) and O(2w), respectively. Hydrogen bonds involving the cis-coordinated O(1w) and O(2w) water molecules [2.913 Å and 154.1°, for O(1w)···O(2w) and O(1w)−H(1w1)···O(2w), respectively] and O(2w) and O(13p) [2.767 Å and 169.0° for O(2w)···O(13p) and O(2w)−H(2w2)···O(13p); $p = 1 - x, 1 - y, -z$] are highlighted in Figure 1. The pyrophosphate group acts as a bis-bidentate ligand forming two six-membered chelate rings with an envelope conformation. The Cu(1)···Cu(2) distance is 4.646 Å whereas the shortest interdimer Cu···Cu separations are 5.899 [Cu(2)···Cu(2p)] and 6.057 Å [Cu(1)···Cu(1q); $q = 1 - x, 1 - y, 1 - z$]. Intermolecular $\pi-\pi$ interactions from adjacent H-bonded chains (interplanar distance between adjacent bipy's is 3.5 Å) through an interleaving of bipy ligands in the *yz* plane leads to a layer containing Cu(II) dimers. Further $\pi-\pi$ interactions are also present along the *y*-axis (Figure 1), which results in the formation of a three-dimensional network.

---

† Trinity College Dublin.

‡ Universitat de València.

§ Queen's University.

[1] (a) Walker, J. E. *Angew. Chem.* **1998**, *110*, 2438; *Angew. Chem., Int. Ed.* **1998**, *37*, 2308. (b) Boyer, P. D. *Angew. Chem.* **1998**, *110*, 2424; *Angew. Chem., Int. Ed.* **1998**, *37*, 2296.

[2] (a) *The Biochemistry of Nucleic Acids*, 10th ed.; Adams, R. L. P., Knowler, J. T., Leader, D. P., Eds.; Chapman and Hall: New York, 1986. (b) *Nucleic Acids in Chemistry and Biology*, 2nd ed.; Blackburn, G. M., Gait, M. J., Eds.; Oxford University Press: 1996.

[3] Lipscomb, W. N.; Sträter, N. *Chem. Rev.* **1996**, *96*, 2375 and references therein.

[4] (a) Wilcox, D. E. *Chem. Rev.* **1996**, *96*, 2435. (b) Welsh, K. M.; Cooperman, B. S. *Biochemistry* **1983**, *22*, 2243. (c) Heikinheimo, P.; Pohjanjoki, P.; Helminen, A.; Tasanen, M.; Cooperman, B. S.; Goldman, A.; Lahti, R. *Eur. J. Biochem.* **1996**, *239*, 138.

[5] Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M.; Murray, K. S. *Inorg. Chim. Acta* **1992**, *197*, 107.

[6] Herron, N.; Thorn, D. L.; Harlow, R. L.; Coulston, G. W. *J. Am. Chem. Soc.* **1997**, *119*, 7149.

[7] Crystal data for **1**: $C_{20}H_{34}Cu_2N_4O_{16}P_2$, $M_w = 775.53$, triclinic, space group $P\bar{1}$, $a = 8.246(1)$ Å, $b = 9.478(2)$ Å, $c = 20.013(4)$ Å, $\alpha = 84.71(2)°$, $\beta = 87.77(1)°$, $\gamma = 74.05(1)°$, $V = 1497.4(5)$ Å^3, $Z = 2$, $D_c = 1.720$, g cm^{-3}, $F(000) = 796$, $\mu = 1.607$ mm^{-1}, $T = 293$ K, crystal size 0.47 × 0.34 × 0.18 mm, total reflections 4210, independent reflections 3884, ($R_{int} = 0.0282$) with [$I > 2\sigma(I)$] 3192 observed data and 397 parameters. Siemens P4 four-circle diffractometer using graphite-monochromated Mo Ka radiation, data collection in the range $4° > 2\theta > 50°$ ($-8 \le h \le 0$, $-10 \le k \le 9$, $-21 \le l \le 21$), corrected for Lorentz, polarization, and absorption effects (max, min transmission = 0.941, 0.644). The structure was solved by direct methods due to Sheldrick and refined by full-matrix least squares on F^2 using SHELXL-97 (Sheldrick, G. M., University of Göttingen). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from a difference Fourier map and refined using a riding model with $U_{ij} = 1.2U_{eq}$. Refinement converged with wR2 = 0.1298 for all data and R1 = 0.0482 for $2\sigma(I)$ data. CCDC 136177.

10.1021/ic000782x CCC: $20.00

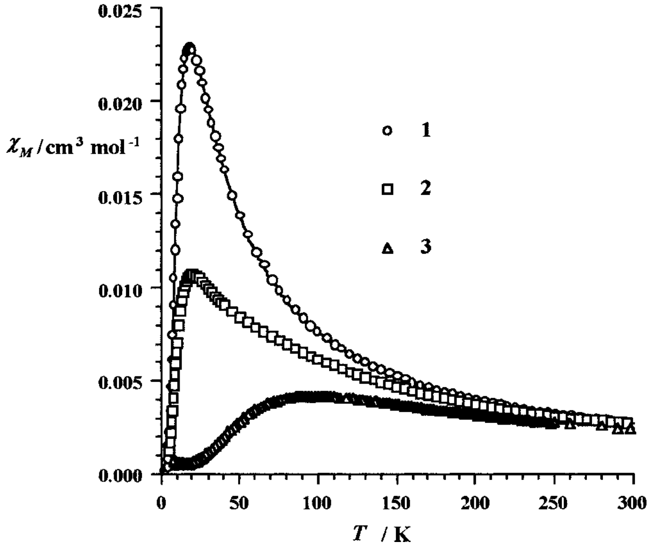

Figure 2. Thermal dependence of χ_M for the compounds **1**−**3** [χ_M being the magnetic susceptibility per two copper(II) ions]. The solid lines are the best fit (see text).

The thermal decomposition of **1** shows that it loses the seven lattice water molecules in the temperature range 25−68 °C, the resulting dihydrated phase (**2**) being stable for 68° < T < 86 °C. The loss of the two coordinated water molecules starts at 86 °C, giving the fully anhydrous compound (**3**) at T > 120 °C, which decomposes at T > 250 °C.[8]

The magnetic behavior[9] of **1**−**3** is shown in Figure 2. The χ_M versus T curves are characteristic of antiferromagnetic coupling with susceptibility maxima at 19 K for **1** and **2**, and 90 K for **3**. From a magnetic point of view, **1** can be described to a first approximation as a Cu(II) chain with regular alternation of two kinds of bridges (pyrophosphato and hydrogen-bonded pathways). The analysis of the susceptibility data of **1** through the Hamiltonian $H = -J\sum_i(\hat{S}_{i-1}\cdot\hat{S}_i - \alpha\hat{S}_{i-1}\cdot\hat{S}_{i+1})$ (α being the alternating parameter and $\hat{S}_i$ the local spin) leads to value of α practically equal to zero. In other words, **1** behaves magnetically as an isolated copper(II) dimer with $J = -20$ cm^{-1}, $g = 2.09$, and $R = 1.2 \times 10^{-6}$.[10] Inspection of the structure shows that the magnetic orbital on each copper atom is of the $d_{x^2-y^2}$ type with the x and y axes being roughly defined by the bonds from copper to bipy nitrogen. The poor overlap between the two non-coplanar copper centered magnetic orbitals through the equatorial O(11)−P(1)−O(14) and O(21)−P(2)−O(23) bridging networks accounts for the weak antiferromagnetic coupling observed. Although there is possibly an additional exchange pathway in **1**, that involving the axially coordinated waters through hydrogen bonding, it would be expected to be much less efficient than the bis-chelating pyrophosphate in mediating exchange interactions. The loss of seven lattice water molecules from **1** to yield **2** (Scheme S1, Supporting Information) causes a decrease in the height of the susceptibility curve while leaving the temperature at which the maximum occurs unchanged. These features are typical of a higher magnetic dimensionality in **2**, indicating that α is now nonzero. It is likely that the loss of lattice water molecules makes easier the approximation of the adjacent pyrophosphate-bridged dinuclear units, reinforcing the $\pi-\pi$ overlap and introducing additional H-bonding to give an alternating two-dimensional magnetic system. The pyrophosphate-bridged copper(II) fragment would remain essentially unchanged (indeed the temperature at which the maximum occurs remains the same), so the magnetic coupling through this bridge is maintained and the additional weaker coupling is assigned to the hydrogen-bonded pathway. Further dehydration leads to compound **3**. Its susceptibility curve exhibits a maximum at 90 K indicating that a stronger antiferromagnetic coupling occurs in **3** and suggesting the formation of a polymeric compound upon dehydration (Scheme S1). This conclusion is further supported by a shift toward lower frequencies of the strongest P−O stretching vibration (ca. 20 cm^{-1}) in the IR spectrum[11] when going from **1** to **2** to **3**. The exchange coupling through the “oxo” bridge (P−O) would be expected to be dominant and strongly antiferromagnetic in nature. Consequently, the magnetic behavior of **3** would be typical of a relatively strongly coupled copper(II) dimer, and this is consistent with the shift of the susceptibility maximum from 19 (**1**) to 90 K (**3**). The analysis of the magnetic behavior of **3** through a simple Bleaney−Bowers expression leads to an excellent fit with $J = -110$ cm^{-1}, $g = 2.08$, and $R = 5.0 \times 10^{-5}$. This relatively strong coupling is in agreement with the proposed “oxo”-bridging pathway (Scheme S1). We recall here that strong antiferromagnetic coupling of up to −300 cm^{-1} has been reported for singly hydroxo bridged copper(II) complexes.[12]

The present work illustrates for the first time the profound influence of pyrophosphate-assisted water loss on magnetic properties and demonstrates that controlled dehydration leads to an increase in magnetic dimensionality.[13] Similar examples of spectacular magnetostructural effects caused by carboxylate-assisted water loss in polynuclear compounds have been reported previously.[14] Extension of this work to incorporate bridging pyrophosphate ligands into other polynuclear assemblies is currently underway.

Acknowledgment. We acknowledge financial support from the Trinity College Academic Development Fund, the HEA Strategic Research Initiative, and the Spanish Dirección General de Investigación Científica y Técnica (DGICYT) (Project PB-97-1397).

Supporting Information Available: Thermal ellipsoid plots of **1** with numbering scheme (Figure S1) and packing diagrams (Figure S2). X-ray crystallographic file in CIF format. Magnetic susceptibility (Figures S3 and S4) and TG-DTA plots (Figure S5). Scheme S1. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000782X

---

(8) See Figure S5, Supporting Information. Satisfactory elemental analyses (C, H, N) were obtained for **1**−**3**.

(9) Magnetic measurements for **1**−**3** were performed on a Quantum Design SQUID susceptometer in the temperature range 1.9−300 K under an applied field $H = 50$ G.

(10) R is the agreement factor defined as $\sum_i[\chi_M^{obs}(i) - \chi_M^{calc}(i)]^2/[\chi_M^{obs}(i)]^2$.

(11) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry*, 5th ed.; Wiley: Chichester, 1997. (b) Corbridge, D. E. C.; Lowe, E. J. *J. Chem. Soc.* **1954**, 493. (c) Hezel, A.; Ross, S. D. *Spectrochimica Acta* **1967**, *23A*, 1583.

(12) Castro, I.; Faus, J.; Julve, M.; Lloret, F.; Verdaguer, M.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Vaisserman, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2207 and references therein.

(13) (a) Kahn, O.; Larionova, J.; Yakhmi, J. V. *Chem.*−*Eur. J.* **1999**, 5, 3443. (b) Pei, Y.; Kahn, O.; Nakatani, K.; Codjovi, E.; Mathoniere, C.; Sletten, J. *J. Am. Chem. Soc.* **1991**, *113*, 6558.

(14) (a) Nakatani, K.; Carriat, J. Y.; Journaux, Y.; Kahn, O.; Lloret, F.; Renard, J. P.; Pei, Y.; Sletten, J.; Verdaguer, M. *J. Am. Chem. Soc.* **1989**, *111*, 5739. (b) Lloret, F.; Julve, M.; Ruiz, R.; Journaux, Y.; Nakatani, K.; Kahn, O.; Sletten, J.; *Inorg. Chem.* **1993**, *32*, 27. (c) Cano, J.; De Munno, G.; Sanz, J. L.; Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Caneschi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1915.