Alcoholysis of 2,2′-Pyridil, $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$, in the Presence of Copper(II): A Family of Planar Pentanuclear Copper(II) Complexes Stabilized by $[(2\text{-}C_5H_4N)C(O)(OR)C(O)(OR)(2\text{-}C_5H_4N)]^{2-}$ and Carboxylate Ligands

Giannis S. Papaefstathiou,† Catherine P. Raptopoulou,‡ Alexandros Tsohos,‡ Aris Terzis,*,‡ Evangelos G. Bakalbassis,*,§ and Spyros P. Perlepes*,†

Department of Chemistry, University of Patras,
265 00 Patras, Greece, Institute of Materials Science, NCSR
“Demokritos”, 153 10 Aghia Paraskevi Attikis, Greece, and
Laboratory of Applied Quantum Chemistry, Department of
Chemistry, Aristotle University of Thessaloniki,
540 06 Thessaloniki, Greece

Received October 4, 1999

Introduction

The development[1] of routes and strategies for the synthesis of high-nuclearity complexes of 3d metals in moderate oxidation states is of great importance because these species have provided substantial impetus for developments in several different fields, including bioinorganic chemistry, magnetochemistry, material chemistry, and solid-state physics.

We have been pursuing studies[2,3] of polynuclear complexes of the later 3d metals because such clusters may display unusual structures and interesting magnetic properties. One of our routes[2] takes advantage of the observation that the reactions between metal carboxylates and di-2-pyridyl ketone [$(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)$; see Chart 1] lead to incomplete replacement of the carboxylate ligands and the formation of large polynuclear arrays of metal ions. The structural diversity of the resultant species stems from the ability of the singly and doubly deprotonated anions of the *gem*-diol form of $(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)$ to adopt a variety of coordination modes, sometimes two different modes in the same complex. Restricting further discussion to copper(II) chemistry, we note that the synthetic investigation of the $[Cu_2(O_2CMe)_4(H_2O)_2]/(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)/ClO_4^-$ reaction mixture in H_2O has led to the isolation of the remarkable octanuclear complex[2a] $[Cu_8\{(2\text{-}C_5H_4N)C(O)(OH)(2\text{-}C_5H_4N)\}_8(O_2CMe)_4](ClO_4)_4$, whereas the reaction of $[Cu_2(O_2CMe)_4(H_2O)_2]$ with $(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)$ in MeCN, in the absence of counterions, gave the novel molecules[2b] $[Cu_7(OH)_2\{(2\text{-}C_5H_4N)CO_2(2\text{-}C_5H_4N)\}_3(O_2CMe)_6]$ and $[Cu_{12}\{(2\text{-}C_5H_4N)CO_2(2\text{-}C_5H_4N)\}_6(O_2CMe)_{12}]$.

More recently, our efforts have turned toward the use of 2,2′-pyridil [$(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$; Chart 1], which presents chemical similarities to $(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)$ but contains an extra donor group, to see how incorporation of this ligand type might affect the structures and physical properties of the products. Here we report a study of a simple reaction involving a “blend” of $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ and carboxylate ligands in alcohols, which produces a series of planar pentanuclear copper(II) complexes. The structures of three members of this family and the magnetic properties of one representative complex are described. This work can also be regarded as a contribution to the almost unexplored coordination chemistry of 2,2′-pyridil.[4]

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials and solvents as received (Aldrich Co.). The compound $Cu(O_2CPh)_2\cdot EtOH$ was prepared as described elsewhere.[5]

$[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OEt)C(O)(OEt)(2\text{-}C_5H_4N)\}_2(O_2CMe)_4(EtOH)_2]\cdot 2EtOH$ (1). To a solution of $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ (0.12 g, 0.56 mmol) in EtOH (10 mL) was added a solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (0.28 g, 0.70 mmol) in the same solvent (30 mL). The blue solution obtained was stirred at ambient temperature for 30 min and allowed to stand undisturbed for 3 d. Well-formed, X-ray-quality crystals of **1** slowly appeared. The blue prismatic crystals were collected by filtration, washed with EtOH, and dried in air. The yield was ∼45% based on copper. Anal. Calcd for $C_{48}H_{74}Cu_5N_4O_{22}$: C, 41.87; H, 5.41; N, 4.07; Cu, 23.07. Found: C, 41.70; H, 5.36; N, 4.22; Cu, 22.47. Selected IR data (cm^{-1}) (KBr pellet): 3444 (m, br), 1590 (s), 1474 (m), 1408 (s), 1124 (m), 1092 (s), 1022 (m), 772 (m), 656 (m).

$[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OPr^n)C(O)(OPr^n)(2\text{-}C_5H_4N)\}_2(O_2CMe)_4(Pr^nOH)_2]\cdot 0.8Pr^nOH$ (2). To a stirred solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (0.14 g, 0.35 mmol) in Pr^nOH (20 mL) was added a solution of $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ (0.06 g, 0.28 mmol) in the same solvent (10 mL). Layering of Et_2O

---

† University of Patras.

‡ NCSR “Demokritos”.

§ Aristotle University of Thessaloniki.

(1) (a) Libby, E.; Folting, K.; Huffman, C. J.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2549. (b) Winpenny, R. E. P. *Comments Inorg. Chem.* **1999**, *20*, 233. (c) Burger, J.; Klüfers, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 776. (d) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G.-L.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774. (e) Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491. (f) Tandon, S. K.; Thompson, L. K.; Bridson, J. N.; Benelli, C. *Inorg. Chem.* **1995**, *34*, 5507. (g) Real, J. A.; De Munno, G.; Chiappetta, R.; Julve, M.; Lloret, F.; Journaux, Y.; Colin, J.-C.; Blondin, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1184. (h) Murray, K. S. *Adv. Inorg. Chem.* **1995**, *43*, 261. (i) Escuer, A.; Font-Bardia, M.; Kumar, S. B.; Solans, X.; Vicente, R. *Polyhedron* **1999**, *18*, 909.

(2) (a) Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Paschalidou, S.; Perlepes, S. P.; Bakalbassis, E. G. *Inorg. Chem.* **1997**, *36*, 3996. (b) Tangoulis, V.; Raptopoulou, C. P.; Paschalidou, S.; Bakalbassis, E. G.; Perlepes, S. P.; Terzis, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1083. (c) Tangoulis, V.; Raptopoulou, C. P.; Paschalidou, S.; Tsohos, A. E.; Bakalbassis, E. G.; Terzis, A.; Perlepes, S. P. *Inorg. Chem.* **1997**, *36*, 5270. (d) Tsohos, A.; Dionyssopoulou, S.; Raptopoulou, C.; Terzis, A.; Bakalbassis, E. G.; Perlepes, S. P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 983.

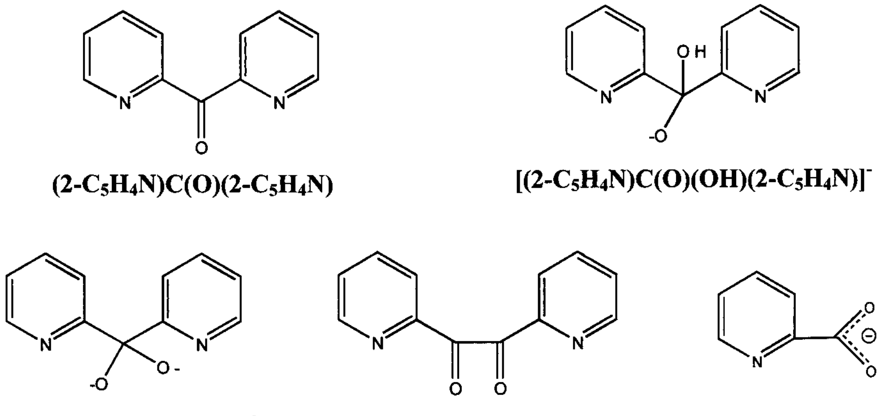
(3) (a) Bakalbassis, E. G.; Diamantopoulou, E.; Perlepes, S. P.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Zafiropoulos, Th. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1347. (b) Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Bakalbassis, E. G.; Diamantopoulou, E.; Perlepes, S. P. *Inorg. Chem.* **1998**, *37*, 3142. (c) Tangoulis, V.; Diamantopoulou, E.; Bakalbassis, E. G.; Raptopoulou, C. P.; Terzis, A.; Perlepes, S. P. *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 463.

(4) (a) Black, D. S. C. *Chem. Commun.* **1967**, 311. (b) Black, D. S. C.; Srivastava, R. C. *Aust. J. Chem.* **1969**, *22*, 1439. (c) Black, D. S. C.; Srivastava, R. C. *Aust. J. Chem.* **1970**, *23*, 2067. (d) Barandika, M. G.; Serna, Z. E.; Urtiaga, M. K.; De Larramendi, J. I. R.; Arriortua, M. I.; Cortes, R. *Polyhedron* **1999**, *18*, 1311. (e) Abrahams, B. F.; Hoskins, B. F.; Hudson, T. A.; Robson, R. *Acta Crystallogr., Sect. C* **2000**, *56*, e126.

(5) Inoue, M.; Kishita, M.; Kubo, M. *Inorg. Chem.* **1964**, *3*, 239.

10.1021/ic991169k CCC: $19.00

Chart 1. Ligands Discussed in the Text[a]



$(2\text{-}C_5H_4N)C(O)(2\text{-}C_5H_4N)$

$[(2\text{-}C_5H_4N)C(O)(OH)(2\text{-}C_5H_4N)]^-$

$[(2\text{-}C_5H_4N)CO_2(2\text{-}C_5H_4N)]^{2-}$

$(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$

pic$^-$

[a] Note that $[(2\text{-}C_5H_4N)C(O)(OH)(2\text{-}C_5H_4N)]^-$ and $[(2\text{-}C_5H_4N)CO_2(2\text{-}C_5H_4N)]^{2-}$ do not exist as free species but exist only in their complexes.

Table 1. Crystallographic Data for Complexes **1**−**3**

parameter	**1**	**2**	**3**
formula	$C_{48}H_{74}Cu_5N_4O_{22}$	$C_{52.4}H_{80.4}Cu_5N_4O_{20.8}$	$C_{72}H_{90}Cu_5N_4O_{22}$
fw	1376.81	1416.91	1681.24
space group	$P\bar{1}$	$I2/a$	$P\bar{1}$
a, Å	12.522(1)	25.12(1)	12.488(5)
b, Å	11.117(1)	16.450(7)	12.200(5)
c, Å	12.643(1)	17.254(7)	15.373(6)
α, deg	65.43(1)		111.29(1)
β, deg	81.49(1)	92.32(1)	92.93(1)
γ, deg	74.34(1)		114.33(1)
V, Å^3	1539.9(3)	7123(5)	1932.1(1)
Z	1	4	1
T, °C	25	25	25
λ, Å	1.541 80	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.485	1.321	1.444
μ, mm^{-1}	2.539	1.533	1.427
R1[a]	0.0381	0.0683	0.0458
wR2[a]	0.1011	0.1736	0.0966

[a] $w = 1/[\sigma^2(F_o2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$; α = 0.0504, $b = 1.1669$ for **1**, $a = 0.0843$, $b = 70.5315$ for **2**, and $a = 0.0000$, $b = 2.4010$ for **3**. $R1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for 4350 (**1**), 3065 (**2**), and 5258 (**3**) reflections with $I > 2\sigma(I)$.

(45 mL) over the dark blue solution gave a mixture of mauve needles and blue prismatic crystals. These were carefully collected by filtration. The two products were readily separated manually, and the mauve and blue crystals were determined by single-crystal X-ray crystallography to be *trans*-[Cu(pic)$_2$] (pic$^-$ = picolinate ion) and complex **2**, respectively. The crystals of **2** were washed with Et_2O and dried in air; typical yields were in the 10−15% range (based on Cu). Anal. Calcd for $C_{52.4}H_{80.4}Cu_5N_4O_{20.8}$: C, 44.41; H, 5.71; N, 3.95; Cu, 22.42. Found: C, 44.19; H, 5.55; N, 3.98; Cu, 23.00. Selected IR data (cm^{-1}) (KBr pellet): 3470 (m), 3444 (m, br), 1588 (s), 1570 (m), 1396 (s), 1120 (m), 1092 (s), 1034 (m), 770 (m), 656 (m).

$[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OEt)C(O)(OEt)(2\text{-}C_5H_4N)\}_2(O_2CPh)_4(EtOH)_2]\cdot 2Et_2O$ (3). Solid $Cu(O_2CPh)_2\cdot EtOH$ (0.13 g, 0.37 mmol) was dissolved with stirring in a solution of $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ (0.04 g, 0.19 mmol) in EtOH (30 mL) at room temperature. The blue solution obtained was filtered and layered with Et_2O (40 mL). Slow mixing yielded mauve needles of *trans*-[Cu(pic)$_2$] and blue prismatic crystals of **3**. The X-ray-quality blue crystals were separated manually from the mixture, washed with copious amounts of Et_2O, and dried in air. The yield was ~10% (based on Cu). An analysis sample gave results consistent with $[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OEt)C(O)(OEt)(2\text{-}C_5H_4N)\}_2(O_2CPh)_4(EtOH)_2]$. Anal. Calcd for $C_{64}H_{70}Cu_5N_4O_{20}$: C, 50.14; H, 4.60; N, 3.65; Cu, 20.72. Found: C, 49.87; H, 4.70; N, 3.59; Cu, 20.96. Selected IR data (cm^{-1}) (KBr pellet): 3446 (m, br), 1606 (s), 1568 (s), 1382 (s), 1366 (s), 1116 (m), 1084 (s), 960 (m), 768 (w), 656 (w).

Physical Techniques. C, H, and N microanalyses were conducted by the microanalytical service of the University of Ioannina, Greece, and copper analysis was carried out by EDTA titration. IR spectra (4000−500 cm^{-1}) were recorded on a Perkin-Elmer 16 PC spectrometer. Magnetic susceptibility measurements were carried out on a polycrystalline sample of **1** in the 3−300 K range under a magnetic field of 6 kG by using a Quantum Design SQUID susceptometer. The susceptibility of the sample was found to be field independent. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Solid-state EPR spectra in the 5−300 K temperature range were recorded on a Bruker ER 200D-SRC X-band spectrometer, equipped with an Oxford ESR 9 helium continuous-flow cryostat, a Hall probe, and a Hewlett-Packard frequency meter.

X-ray Crystallography. Blue prismatic crystals of **1**−**3** were mounted in capillaries filled with drops of the mother liquors. Complete crystal data and parameters for data collection for the three complexes are reported in Table 1. Intensity data were recorded using a $\theta-2\theta$ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization, and ψ-scan absorption (only for **1**) corrections were applied using Crystal Logic^n software. The structures were solved by direct methods using SHELXS-86[6a] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93.[6b] Further crystallographic details are briefly as follows. Complex **1**: $2\theta(\max) = 130°$ (Cu Kα radiation), scan speed 3.0°/min, scan range $2.4° + \alpha_1\alpha_2$ separation, reflections collected/unique/used = 5464/5207 ($R_{\text{int}} = 0.0180$)/5207, 432 parameters refined, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.444/-0.548$ e/Å^3, $(\Delta/\sigma) = 1.295$. Complex **2**: $2\theta(\max) = 45°$ (Mo Kα radiation), scan speed 1.5°/min, scan range $2.1° + \alpha_1\alpha_2$ separation, reflections collected/unique/used = 4290/4635 ($R_{\text{int}} = 0.0360$)/4635, 377 parameters refined, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.623/-0.487$ e/Å^3, $(\Delta/\sigma) = 0.124$. Complex **3**: $2\theta(\max) = 50°$ (Mo Kα radiation), scan speed 2.5°/min, scan range $2.2° + \alpha_1\alpha_2$ separation, reflections collected/unique/used = 7161/6807 ($R_{\text{int}} = 0.0322$)/6651, 615 parameters refined, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.458/-0.338$ e/Å^3, $(\Delta/\sigma) = 0.738$. For **1**, all hydrogen atoms of the methyl groups of the ligand and the acetates, as well as hydrogens of the coordinated and solvated EtOH molecules, were introduced at calculated positions as riding on bonded atoms; the same was true for the hydrogen atoms on C(36), C(37), and C(38) in **3**. The remainder of the hydrogen atoms in **1** and **3** were located by difference maps and refined isotropically. All hydrogens of **2** were introduced at calculated positions. All non-hydrogen atoms of **1** and **3** were refined anisotropically. For **2**, the methylene carbon C(26) of the coordinated Pr^nOH molecule was found to be disordered and was refined isotropically in two orientations with occupancy fixed at 50%; the methyl group of the coordinated solvent [C(27)] was refined isotropically, as was that of the solvate Pr^n-OH, which diffused during data collection and refined with occupation factors fixed at 10.4. The remainder of the non-hydrogen atoms were refined anisotropically.

Results and Discussion

Syntheses. The preparations of compounds **1**−**3** can be achieved via the reactions of $[Cu_2(O_2CMe)_4(H_2O)_2]$ or $Cu(O_2CPh)_2\cdot EtOH$ with 2,2′-pyridil in EtOH (**1**, **3**) or Pr^nOH (**2**) at room temperature. The preparation of the representative complex **1** is summarized in eq 1. The copper(II)-mediated alcoholysis

$$5[Cu_2(O_2CMe)_4(H_2O)_2] + 4(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N) + 16EtOH \xrightarrow[20\,°C]{EtOH} 2[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OEt)C(O)(OEt)(2\text{-}C_5H_4N)\}_2(O_2CMe)_4(EtOH)_2]\cdot 2EtOH + 12MeCO_2H + 6H_2O \tag{1}$$

of $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ to give the dianions of bis(hemiacetals) $(2\text{-}C_5H_4N)C(OH)(OR)C(OH)(OR)(2\text{-}C_5H_4N)$ involves a nucleophilic attack of ROH molecules on the carbonyl groups. In such reactions, it might not be necessary for the carbonyl groups to be coordinated to the metal center; the induced polarization from more remote coordination sites, i.e., the pyridyl nitrogen atoms, might be sufficient.[7] There are few examples in which a ketone group in a polydentate ligand is attacked by alcohols in the presence of metal ions, the well studied example being that of di-2-pyridyl ketone.[2c,7,8]

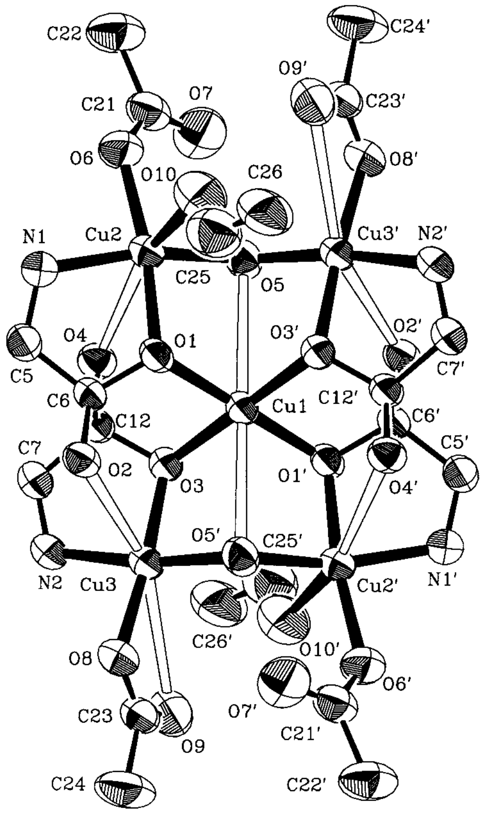


Figure 1. ORTEP view of the representative complex $[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OEt)C(O)(OEt)(2\text{-}C_5H_4N)\}_2(O_2CMe)_4(EtOH)_2]\cdot 2EtOH$ (**1**), with 50% thermal ellipsoids, showing the atom-labeling scheme. The lattice EtOH molecules are not shown. Primes are used for symmetry-related atoms. For clarity, all carbon atoms of the −OEt groups of the organic ligand and most aromatic carbon atoms have been omitted. The μ_3-OH^- oxygen atoms are O(5) and O(5′), and the −OEt oxygen atoms are O(2), O(4), O(2′), and O(4′), while carbon atoms C(5), C(7), C(5′), and C(7′) belong to the pyridyl rings; see also Chart 2.

The following points are of synthetic interest: (i) The reaction of $[Cu_2(O_2CMe)_4(H_2O)_2]$ or $Cu(O_2CPh)_2\cdot EtOH$ with $(2\text{-}C_5H_4N)C(O)C(O)(2\text{-}C_5H_4N)$ in MeOH leads to a mixture of mauve crystals of *trans*-$[Cu(pic)_2]$ and blue crystals of *trans*-$[Cu(pic)_2]\cdot 2H_2O$.[9] This observation was also made by Black and Srivastava, who proposed a mechanism for the reaction.[4c] (ii) The planar pentanuclear complexes can be isolated either as a pure product (**1**) or in a mixture with *trans*-$[Cu(pic)_2]$ (**2**, **3**) *only* in higher alcohols (EtOH, Pr^nOH). (iii) The temperature is a particularly important synthetic parameter. If the reaction mixtures in EtOH or Pr^nOH are heated or refluxed, they yield exclusively *trans*-$[Cu(pic)_2]$ or/and *trans*-$[Cu(pic)_2]\cdot 2H_2O$.

Description of the Structures. Although complexes **1**−**3** are not isostructural (see Table 1), their molecular structures are similar. A labeled ORTEP plot of the representative complex **1**, whose structure will be discussed in detail, is shown in Figure 1, and selected interatomic distances and angles for this compound are listed in Table 2.

---

(6) (a) Sheldrick, G. M. *SHELXS-86*: *Structure Solving Program*; University of Göttingen: Göttingen, Germany, 1986. (b) Sheldrick, G. M. *SHELXL-93*: *Crystal Structure Refinement Program*; University of Göttingen: Göttingen, Germany, 1993.

(7) Constable, E. W. *Metals and Ligand Reactivity*, 2nd ed.; VCH: Weinheim, Germany, 1996: pp 46−48, 57−59.

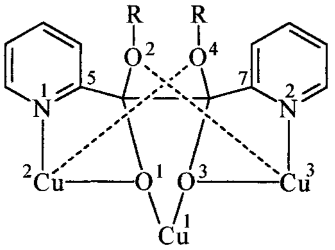
(8) (a) Deveson, A. C.; Heath, S. L.; Harding, C. J.; Powell, A. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3173. (b) Papadopoulos, A.; Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Kessissoglou, D. P. *Inorg. Chem.* **1996**, *35*, 559. (c) Kavounis, C. A.; Tsiamis, C.; Cardin, C. J.; Zubavichus, Y. *Polyhedron* **1996**, *15*, 385. (d) Manzur, J.; Garcia, A. M.; Garland, M. T.; Acuna, V.; Gonzáles, O.; Pena, O.; Atria, A. M.; Spodine, E. *Polyhedron* **1996**, *15*, 821. (e) Alonzo, G.; Bertazzi, N.; Maggio, F.; Benetollo, F.; Bombieri, G. *Polyhedron* **1996**, *15*, 4269. (f) Baggio, R.; Gonzáles, O.; Garland, M. T.; Manzur, J.; Acuna, V.; Atria, A. M.; Spodine, E.; Pena, O. *J. Cryst. Spectrosc. Res.* **1993**, *23*, 749. (g) Alonzo, G.; Bertazzi, N.; Bombieri, G.; Bruno, G. *J. Chem. Soc., Dalton Trans.* **1987**, 2337.

(9) Segl'a, P.; Jamnicky, M.; Koman, M.; Sima, J.; Glowiak, T. *Polyhedron* **1998**, *17*, 4525.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in the Representative Pentanuclear Complex **1**

Cu(1)···Cu(2)	3.263(1)	Cu(2)−N(1)	1.993(3)
Cu(1)···Cu(3)	3.222(1)	Cu(2)−O(1)	1.999(2)
Cu(2)···Cu(3)	5.533(1)	Cu(2)···O(4)	2.777(2)
Cu(2)···Cu(3′)	3.382(1)	Cu(3)−O(8)	1.940(2)
Cu(1)−O(1)	1.948(2)	Cu(3)···O(9)	2.869(2)
Cu(1)−O(3)	1.941(2)	Cu(3)−O(5′)	1.890(2)
Cu(1)···O(5)	2.764(2)	Cu(3)−N(2)	1.981(3)
Cu(2)−O(5)	1.909(2)	Cu(3)−O(3)	1.993(2)
Cu(2)−O(6)	1.951(2)	Cu(3)···O(2)	2.582(2)
Cu(2)−O(10)	2.417(3)		
Cu(1)−O(1)−Cu(2)	111.5(1)	O(1)−Cu(2)−O(6)	170.6(1)
Cu(1)−O(3)−Cu(3)	109.9(1)	O(4)···Cu(2)−N(1)	75.8(1)
Cu(1)−O(5)−Cu(2)	86.6(1)	O(4)···Cu(2)−O(10)	159.6(1)
Cu(1)−O(5)−Cu(3)	85.4(1)	O(2)···Cu(3)−O(3)	72.3(1)
Cu(2)−O(5)−Cu(3′)	125.8(1)	O(2)···Cu(3)−O(5′)	95.9(1)
O(1)−Cu(1)−O(3)	85.0(1)	O(2)···Cu(3)···O(9)	155.3(1)
O(1)−Cu(1)···O(5)	69.9(1)	O(3)−Cu(3)−O(5′)	90.8(1)
O(3)−Cu(1)···O(5′)	69.5(1)	O(3)−Cu(3)−O(8)	175.2(1)
O(5)−Cu(2)−O(6)	98.6(1)	O(5′)−Cu(3)−N(2)	171.2(1)
O(5)−Cu(2)−N(1)	163.0(1)	O(5′)-Cu(3)−O(9)	93.7(1)
O(1)−Cu(2)−O(10)	91.8(1)	O(8)···Cu(3)−O(9)	50.3(1)

Chart 2. Coordination of $[(2\text{-}C_5H_4N)C(O)(OR)C(O)(OR)(2\text{-}C_5H_4N)]^{2-}$ in Complexes **1−3**[a]



[a] The atomic labeling scheme corresponds to that used in Figure 1.

The pentanuclear assembly $[Cu_5(OH)_2\{(2\text{-}C_5H_4N)C(O)(OR)C(O)(OR)(2\text{-}C_5H_4N)\}_2(O_2CR')_4(ROH)_2]$ of **1−3** (R = Et, Pr^n; R′ = Me, Ph) is composed of a rectangular arrangement of four Cu^{II} atoms [Cu(2), Cu(3), Cu(2′), Cu(3′)] centered on the fifth [Cu(1)]. The central metal site lies on a crystallographic inversion center, and thus, all the copper atoms are coplanar. The distances from the central Cu^{II} atom to the peripheral ions average to 3.24 Å in **1**, 3.27 Å in **2**, and 3.23 Å in **3**. The lengths of the short Cu···Cu edges of the rectangle are 3.382(1), 3.318(2), and 3.372(1) Å for **1−3**, respectively; the lengths of the long ones are 5.533(1), 5.632(2), and 5.523(1) Å, respectively. The Cu^{II} atoms at each short edge of the rectangle are bridged by an OH^- ion, which also interacts weakly [Cu(1)···O(5) = 2.764(2) Å in **1**, 2.802(6) Å in **2**, and 2.709(3) Å in **3**] with the central metal. The $[(2\text{-}C_5H_4N)C(O)(OR)C(O)(OR)(2\text{-}C_5H_4N)]^{2-}$ ions behave as $\eta^1{:}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1$ μ_3 ligands (Chart 2). Each ligand spans a long edge of the Cu_4 rectangle and is ligated to the central metal, Cu(1), through both of its deprotonated hydroxy oxygen atoms. The Cu−OR distances are long, suggesting weak interactions, with the Cu(2)···O(4) distances [2.770(3)−2.939(6) Å] being longer than the Cu(3)···O(2) distances [2.582(2)−2.693(6) Å]. A terminal ROH molecule and a monodentate RCO_2^- ligand complete coordination at Cu(2) and its symmetry-related partner [Cu(2′)]. The remaining terminal coordination sites on Cu(3) and Cu(3′) are occupied by chelating RCO_2^- groups; these groups are asymmetrically ligated [Cu(3)−O(8) = 1.932(3)−1.954(7), Cu(3)···O(9) = 2.868(9)−2.981(3) Å]. The crystal structures are stabilized by intra- and intermolecular hydrogen bonds.

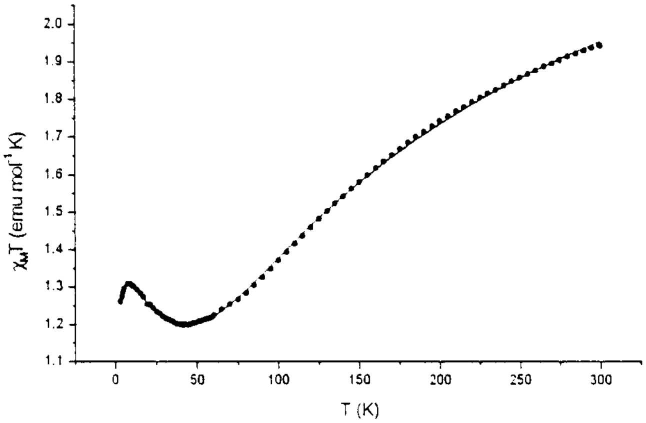


Figure 2. Plot of $\chi_M T/Cu^{II}_5$ vs T for a polycrystalline sample of **1**. The solid line represents the fit to the theoretical model; see the text for the fitting parameters.

Assuming that the Cu(1)−O(5), Cu(2)−O(4), Cu(3)−O(2), and Cu(3)−O(9) distances represent weak bonding interactions, the copper(II) centers have distorted octahedral coordination geometries with $Cu(1)O_6$, $Cu(2)NO_5$, and $Cu(3)NO_5$ chromophores. Alternatively, Cu(1), Cu(2), and Cu(3) are four-, five-, and four-coordinate, respectively; the four-coordination sites have a perfect [Cu(1)] or a distorted [Cu(3)] square planar geometry, while the five-coordinate site can be described as distorted square pyramidal with the apical site occupied by O(10). The Cu−OH−Cu angle involving the outer metal ions of the pentanuclear core is in the range 121.1(3)-125.8(1)°, while those around the central copper are in the range 85.4(1)-87.5(1)°.

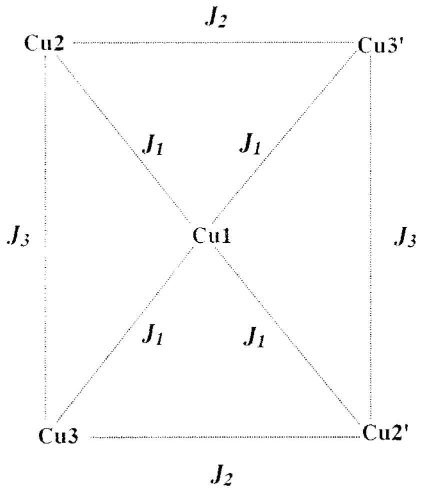
Compounds **1−3** are the first structurally characterized complexes of *any* metal containing the dianions $[(2\text{-}C_5H_4N)C(O)(OR)C(O)(OR)(2\text{-}C_5H_4N)]^{2-}$ as ligands. They join a very small class of discrete Cu^{II} clusters of nuclearity 5;[10] two members of this class have planar arrangements for the five metal ions.[10e] The $[Cu_5(OH)_2]^{8+}$ core found in **1−3** is also present in the complexes $Cu_5(OH)_2L_2(NO_3)_4{\cdot}2.5H_2O$ [L^{2-} = the dianion of 3,6-bis((4-methylpiperazino)methyl)pyrocatechol],[10a] $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)_4](ClO_4)_2$ (Him = imidazole),[10e] and $[Cu_5(OH)_2(O_2CMe)_6(1\text{-}Meim)_4](ClO_4)_2$ (1-Meim = 1-methylimidazole).[10e]

Magnetic Properties of 1. The magnetic behavior (3−300 K) of a powder sample of the representative complex **1** in the form of a χ_M T versus T plot is shown in Figure 2 (χ_M is the corrected molar magnetic susceptibility per pentamer). The room-temperature value of χ_M T (1.94 emu mol^{-1} K) is smaller than expected for five uncoupled $S = {}^1/_2$ spins (2.1 emu mol^{-1} K for $g = 2.1$), indicative of antiferromagnetic coupling, even at 300 K. The product decreases rapidly with decreasing temperature down to 45 K, where it displays a minimum; the value at 45 K (1.2 emu mol^{-1} K) is what is expected for three uncoupled $S = {}^1/_2$ spins. Below 45 K, the product increases and exhibits a maximum (1.3 emu mol^{-1} K) at ca. 7 K.

---

(10) (a) Gojon, E.; Gaillard, J.; Latour, J.-M.; Laugier, J. *Inorg. Chem.* **1987**, *26*, 2046. (b) Kurzak, B.; Farkas, E.; Glowiak, T.; Kozlowski, H. *J. Chem. Soc., Dalton Trans.* **1991**, 163. (c) Handley, J.; Collison, D.; Garner, C. D.; Helliwell, M.; Docherty, R.; Lawson, J. R.; Tasker, P. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1036. (d) Gibney, B. R.; Kessissoglou, D. P.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1994**, *33*, 4840. (e) Meenakumari, S.; Lakshminarayanan, M.; Tiwary, S. K.; Chakravarty, A. R. *Inorg. Chem.* **1995**, *34*, 5091. (f) Doyle, A. A.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 2131. (g) Murrie, M.; Collison, D.; Garner, C. D.; Helliwell, M.; Tasker, P. A.; Turner, S. S. *Polyhedron* **1998**, *17*, 3031.

Chart 3. Exchange Pathways in **1**



A careful inspection of the crystal structure of **1** clearly demonstrates that three exchange integrals, J_1, J_2, and J_3 (see Chart 3), are required to model the data properly. If we assume that S_1, S_2, S_3, $S_{2'}$, and $S_{3'}$ correspond to the spin operators of Cu(1), Cu(2), Cu(3), Cu(2′), and Cu(3′) magnetic centers, respectively, then the isotropic HDvV Hamiltonian for the system of five spins under study should be as follows:

$$H = -2J_1S_1(S_2 + S_3 + S_{2'} + S_{3'}) - 2J_2(S_2{\cdot}S_{3'} + S_{2'}{\cdot}S_3) - 2J_3(S_2{\cdot}S_3 + S_{2'}{\cdot}S_{3'}) \quad (2)$$

The theoretical expression for the magnetic susceptibility used to fit the data is

$$\chi_{\mathrm{M}} = \frac{N\beta^2 g^2 \sum_n m_n^{\,2} \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \quad (3)$$

where $m_n = m_1 + m_2 + m_3 + m_4 + m_5$ for the *n*th level. Since J_3 is expected to be small—due to the very long Cu(2)···Cu(3) distance of 5.533(1) Å—a first fit of the 3−300 K data to the above equation was performed by using a two-*J* model. Although the model represented the experimental data of the high-temperature range well, it failed to give a low-temperature fit. However, a three-*J* model for the whole temperature range yielded $J_1 = -37.9$ cm^{-1}, $J_2 = -16.8$ cm^{-1}, $J_3 = -2.7$ cm^{-1}, and $g = 2.09$ ($R = \sum_n[(\chi_{\mathrm{M}}T)_{\mathrm{exptl}} - (\chi_{\mathrm{M}}T)_{\mathrm{calcd}}]^2/\sum_n(\chi_{\mathrm{M}}T)_{\mathrm{exptl}}^{\,2} = 1.0 \times 10^{-5}$). This excellent fit is shown in Figure 2. The ground state ($m_S = \pm{}^3/_2$), predicted by this model, has the central spin up and the four others down, or vice versa, in close agreement with the $\chi_{\mathrm{M}}T$ value at 45 K. Although all *J*'s are negative, the ground state does not correspond to an $m_S = {}^1/_2$ value because of spin frustration, as one would expect from the geometry of the molecule.

The powder EPR spectrum of **1** at 4.5 K shows a multiple line centered at $g = 2.05$, displaying hyperfine interactions and assigned to residual monomeric species, and a less intense line at $g = \sim 4.3$. The latter is characteristic of an effective $S = {}^3/_2$ ground state. The hyperfine-splitting-tensor components deduced from this spectrum are $A_{\parallel} = 190 \times 10^{-4}$ cm^{-1} and $A_{\perp} < 10 \times 10^{-4}$ cm^{-1}.

In an attempt to probe more deeply into the exchange interactions of **1**, its magnetic behavior is closely correlated with its molecular structure. The structure of **1** is built from four coplanar Cu$^{\mathrm{II}}$ ions forming two triangles with a common vertex which is the position of the central metal ion. All five Cu$^{\mathrm{II}}$ ions in the rectangle exhibit distorted six-coordinate geometries. Therefore, the unpaired electron around each of the magnetic centers is described by a ($x^2 - y^2$)-type magnetic orbital pointing from the metal toward its corresponding four nearest-neighboring atoms. Consequently, the spin densities on O(1) and O(1′), belonging to two neighboring magnetic orbitals, should be different from zero, and this should also be the case with the O(3) and O(3′) bridging atoms. However, no definite magnetostructural correlations has been established for the hydroxo- or alkoxo- monobridged dicopper(II) complexes; this is also the case for the mixed hydroxo- and alkoxo-dibridged complexes. As far as the Cu(1)···Cu(2) and Cu(1)···Cu(3) exchange interactions J_1 are concerned, due to the nature of the Cu(1)-centered magnetic orbital, involving the four nearest neighboring atoms [O(1), O(1′), O(3), O(3′)], there is no spin density on the second bridging atom [O(5), O(5′)] coming from the Cu(1)-centered magnetic orbital. Therefore, in contrast to the molecular structure of **1** (see Figure 1), of the two bridging pathways between Cu(1) and Cu(2), only the alkoxo group can propagate the magnetic exchange interactions between them. Moreover, there is also only one bridge, this being the hydroxo group involving O(5), that propagates the magnetic exchange interactions between Cu(2) and Cu(3′). However, the triply bridging function of this single bridge, as compared to the doubly bridging function of the alkoxo bridge mentioned above, could account well for the weaker interaction calculated for J_2 as compared to J_1. Finally, the long Cu(2)···Cu(3) distance of 5.533(1) Å, along with the noncoplanarity of the intervening multiatomic bridge, could account well for the weak antiferromagnetic interaction (J_3) derived from the fitting procedure.

Conclusions

The copper(II) carboxylate/(2-C_5H_4N)C(O)C(O)(2-C_5H_4N) chemistry described here has fulfilled its promise as a source of polynuclear complexes with interesting structures and properties. Although the outcome of this reaction system was unpredictable, it is clear that the bis(hemiacetal) nature of the [(2-C_5H_4N)C(O)(OR)C(O)(OR)(2-C_5H_4N)]$^{2-}$ ions makes them versatile ligands for use with a variety of metals.

Acknowledgment. This work was supported by the Research Committee of the University of Patras (K. Caratheodory Program No. 1941; S.P.P.), the Greek General Secretariat of Research and Technology (Platon Program 1583; E.G.B.), and the Greek Secretariat of Athletics, OPAP (A.T.).

Supporting Information Available: A table of magnetic vs temperature data for **1**, an EPR spectrum at 4.5 K for **1**, and X-ray crystallographic files, in CIF format, for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991169K