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Article

Synthesis, Crystal Structure, and Spectroscopic Characterization of *trans*-Bis[(μ-1,3-bis(4-pyridyl)propane)(μ-(3-thiopheneacetate-*O*))-(3-thiopheneacetate-*O*)]dicopper(II), $\{[Cu_2(O_2CCH_2C_4H_3S)_4\mu\text{-}(BPP)_2]\}_n$: From a Dinuclear Paddle-Wheel Copper(II) Unit to a 2-D Coordination Polymer Involving Monatomic Carboxylate Bridges

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From the reaction between a dinuclear paddle-wheel carboxylate, namely $[Cu_2\mu\text{-}(O_2CCH_2C_4H_3S)_4]$ **(1),** and the flexible ligand 1,3-bis(4-pyridyl)propane (BPP) a neutral 2-D coordination polymer $\{[Cu_2(O_2CCH_2C_4H_3S)_4\mu\text{-}(BPP)_2]\}_n$ **(2)** was obtained. Compounds **1** and **2** were characterized by means of elemental analysis, thermal analysis (TG/DSC), vibrational spectroscopy, and electron paramagnetic resonance (EPR). The crystal structure of **2** reveals that each Cu^{II} is coordinated by two nitrogen atoms from different BPP ligands and two 3-thiopheneacetate groups within a distorted square planar geometry in a trans-{N, N, O, O} arrangement. The BPP ligand adopts a TG conformation bridging two copper centers giving rise to a 1-D sinusoidal polymeric chain along the crystallographic *c* axis. Adjacent 1-D chains are extended into a 2-D coordination network through pairs of monatomic carboxylate bridges in direction of the *b* axis. This bridging mode affords centrosymmetric dimeric units Cu_2O_2, and therefore, the copper ions are involved in a CuN_2O_2O' chromophore displaying a (4 + 1) square pyramidal coordination in the resultant 2-D polymeric network. The polycrystalline X-band EPR spectrum of **2** at room temperature is characteristic of a triplet state with nonnegligible zero-field splitting in agreement with the crystal structure. Crystal data for **2**: monoclinic, space group $P2_1/c$, $a = 9.4253(10)$ Å, $b = 10.9373(10)$ Å, $c = 23.6378(10)$ Å, $\beta = 98.733(4)°$, $Z = 2$.

Introduction

Over the past decade, the design and synthesis of polymeric coordination networks has become the most prominent and interdisciplinary branch of inorganic research in the field of supramolecular chemistry.[1] In part, the major interest in this area is the prospect of producing materials with useful chemical and physical properties with regard to potential applications for molecular recognition, host–guest chemistry, catalysis, and optical and magnetic devices.[2] However, since these desired and specific properties are

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(1) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (d) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *222*, 155–192. (e) Lehn, J.-M. *Science* **2002**, *295*, 2400–2403.

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markedly dependent on the coordination network topology, many efforts have been devoted to fundamental structural aspects to understand and control the several factors that affect the self-assembly of supramolecular architectures.[3]

In this context, 1,3-bis(4-pyridyl)propane, namely BPP, is currently employed as a bridging ligand to the construction of several coordination polymers with a wide variety of network topologies and structural motifs.[4] In contrast to the rigid bidentate 4,4′-bipyridyl analogues, BPP is a flexible ligand that can adopt different conformations with respect to relative orientations of CH_2 groups, such as TT, TG, GG, and GG′ (where T = trans and G = gauche),[4k] as can be seen in Chart 1.

On the other hand, dimeric and polynuclear copper(II) carboxylates have received great attention in the studies of exchange-coupling interactions between adjacents metal centers,[5] as well as for their special bioactive and biocatalytic functions.[6] In addition, carboxylate anions exhibit a versatile coordination behavior displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as η^1:η^1:μ_2 bridging ligands in *syn*,*syn*, *syn*,*anti*, and *anti*,*anti* conformations. Another type of coordination mode is the monatomic bridge,[7] in which two metal ions are connected by a single oxygen atom of a carboxylate group. This diversity of coordination modes assumed by carboxylate ligands is shown in Chart 2.

Chart 1

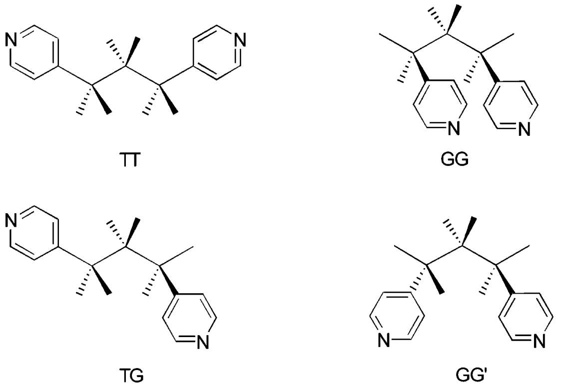
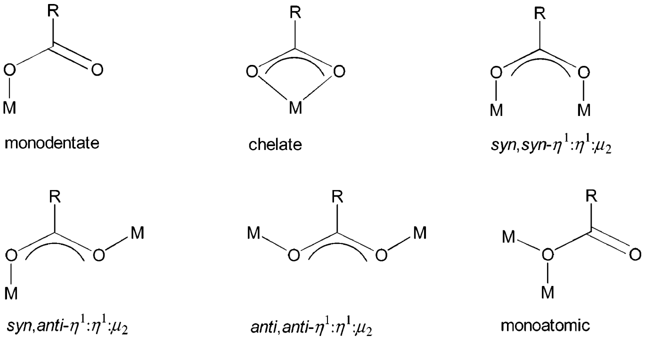


Chart 2



From this point of view, in this work, the synthesis, spectroscopic properties, and crystal structure of a Cu^{II} two-dimensional coordination polymer containing both versatile structural components BPP and carboxylate anions are reported.

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(2) (a) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866−3874. (b) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151−1152. (c) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (d) Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391−1397. (e) Neels, A.; Stoeckli-Evans, H.; Chavan, S. A.; Yakhmi, J. V. *Inorg. Chim. Acta* **2001**, *326*, 106−110. (f) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107−114. (g) Zheng, S.-L.; Tong, M.-L.; Fu, R.-W.; Chen, X.-M.; Ng, S.-W. *Inorg. Chem.* **2001**, *40*, 3562−3569. (h) Hou, H.; Meng, X.; Song, Y.; Fan, Y.; Zhu, Y.; Lu, H.; Du, C.; Shao, W. *Inorg. Chem.* **2002**, *41*, 4068−4075. (i) Du, M.; Chen, S.-T.; Bu, X.-H.; Ribas, J. *Inorg. Chem. Commun.* **2002**, *5*, 1003−1006. (j) Hollingsworth, M. D. *Science* **2002**, *295*, 2410−2413. (k) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511−522. (l) Moulton, B.; Zaworotko, M. J. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117−123.

(3) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562−4569. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117−138. (c) Biradha, K.; Domasevitch, K. V.; Hogg, C.; Moulton, B.; Power, K. N.; Zaworotko, M. J. *Cryst. Eng.* **1999**, *2*, 37−45. (d) Ciurtin, D. M.; Dong, Y.-B.; Smith, M. D.; Barclay, T.; Loye, H.-C. Z. *Inorg. Chem.* **2001**, *40*, 2825−2834. (e) Ni, Z.; Vittal, J. J. *Cryst. Growth Des.* **2001**, *1*, 195−197. (f) Fan, J.; Sui, B.; Okamura, T.-A.; Sun, W.-Y.; Tang, W.-X.; Ueyama, N. *J. Chem. Soc., Dalton Trans.* **2002**, 3868−3873. (g) Ferlay, S.; Koenig, S.; Hosseini, M. W.; Pansanel, J.; Cian, A. D.; Kyritsakas, N. *Chem. Commun.* **2002**, 218−219. (h) Banfi, S.; Carlucci, L.; Caruso, E.; Ciani, G.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **2002**, 2714−2721. (i) Carlucci, L.; Cozzi, N.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Chem. Commun.* **2002**, 1354−1355. (j) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, K.-M.; Lee, S. S. *Inorg. Chem.* **2003**, *42*, 844−850. (k) Du, M.; Bu, X.-H.; Huang, Z.; Chen, S.-T.; Guo, Y.-M. *Inorg. Chem.* **2003**, *42*, 552−559.

(4) (a) Carlucci, L.; Ciani, G.; v. Gudenberg, D. W.; Proserpio, D. M. *Inorg. Chem.* **1997**, *36*, 3812−3813. (b) Batten, S. R.; Jeffery, J. C.; Ward, M. D. *Inorg. Chim. Acta* **1999**, *292*, 231−237. (c) Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2000**, 3065−3073. (d) Carlucci, L.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1506−1510. (e) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 11982−11990. (f) Fu, Z.-Y.; Lin, P.; Du, W.-X.; Chen, L.; Cui, C.-P.; Zhang, W.-J.; Wu, X.-T. *Polyhedron* **2001**, *20*, 1925−1931. (g) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1529−1532. (h) Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Hursthouse, M. B. *Inorg. Chim. Acta* **2001**, *318*, 171−174. (i) Pan, L.; Woodlock, E. B.; Wang, X.; Lam, K.-C.; Rheingold, A. L. *Chem. Commun.* **2001**, 1762−1763. (j) Tong, M.-L.; Wu, Y.-M.; Ru, J.; Chen, X.-M.; Chang, H.-C.; Kitagawa, S. *Inorg. Chem.* **2002**, *41*, 4846−4848. (k) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *CrystEngCommun* **2002**, *4*, 121−129. (l) Jin, K.; Huang, X.; Pang, L.; Li, J.; Appel, A.; Wherland, S. *Chem. Commun.* **2002**, 2872−2873. (m) Gao, E. Q.; Bai. S. Q.; Wang, Z. M.; Yan, C. H. *J. Chem. Soc., Dalton Trans.* **2003**, 1759−1764.

(5) (a) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259−293. (b) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45−83. (c) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1988**, *27*, 3246−3248. (d) Dey, S. K.; Bag, B.; Malik, K. M. A.; El Fallah, M. S.; Ribas, J.; Mitra, S. *Inorg. Chem.* **2003**, *42*, 4029−4035.

(6) (a) Kovala-Demertzi, D.; Theodorou, A.; Demertzis, M. A.; Raptopoulou, C. P.; Terzis, A. *J. Inorg. Biochem.* **1997**, *65*, 151−157. (b) Vaidyanathan, M.; Viswanathan, R.; Palaniandavar, M.; Balasubramanian, T.; Prabhaharan, P.; Muthiah, T. P. *Inorg. Chem.* **1998**, *37*, 6418−6427. (c) Greenaway, F. T.; Riviere, E.; Girerd, J. J.; Labouze, X.; Morgant, G.; Viossat, B.; Daran, J. C.; Roch-Arveiller, M.; Dung, N.-H. *J. Inorg. Biochem.* **1999**, *76*, 19−27. (d) Weder, J. E.; Hambley, T. W.; Kennedy, B. J.; Lay, P. A.; MacLachlan, D.; Bramley, R.; Delfs, C. D.; Murray, K. S.; Moubaraki, B.; Warwick, B.; Biffin, J. R.; Regtop, H. L. *Inorg. Chem.* **1999**, *38*, 1736−1744. (e) Kozlevcar, B.; Leban, I.; Turel, I.; Segedin, P.; Petric, M.; Pohleven, F.; White, A. J. P.; Williams, D. J.; Sieler, J. *Polyhedron* **1999**, *18*, 755−762.

(7) (a) Antolini, L.; Menabue, L.; Saladini, M. *Inorg. Chem.* **1985**, *24*, 1219−1222. (b) Escrivà, E.; Server-Carrió, J.; Lezama, L.; Folgado, J.-V.; Pizarro, J. L.; Ballesteros, R.; Abarca, B. *J. Chem. Soc., Dalton Trans.* **1997**, 2033−2038 and references therein. (c) Ye, B.-H.; Chen, X.-M.; Xue, F.; Ji, L.-N.; Mak, T. C. W. *Inorg. Chim. Acta* **2000**, *299*, 1−8. (d) Mukherjee, P. S.; Maji, T. K.; Mostafa, G.; Ribas, J.; El Fallah, M. S.; Chaudhuri, N. R. *Inorg. Chem.* **2001**, *40*, 928−931.

Experimental Section

Materials and Physical Measurements. 3-Thiopheneacetic acid and 1,3-bis(4-pyridyl)propane were purchased from Aldrich Chemical Co. and used without further purification. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. Copper was measured with an atomic absorption spectrophotometer Hitachi Z-8200. Infrared spectra were recorded on a FT-IR Bomem MB102 spectrometer in the frequency range 4000−400 cm^{-1} using KBr pellets. Thermogravimetric analyses (TG/DTG) were obtained on a TG-50 Mettler STARe. Samples were heated at 10 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 200 mL/min). Differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu DSC50 with a heating rate of 10 °C/min in the temperature range of 25−480 °C. Dynamic nitrogen atmosphere (flow rate = 50 mL/min) was used. Conventional EPR measurements have been done in a custom-built spectrometer equipped with a cylindrical cavity (Bruker) operating at microwave frequencies of 9−11 GHz (X-band) from a 500 mW klystron (Varian). For signal improvement a common 100 kHz field modulation and lock-in detection (EG&G Princeton) have been applied. For the low-temperature measurements a He flux cryosystem (Oxford Instruments) has been used for temperatures in the range from 4 to 300 K. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used for calibration of g values, $g_{DPPH} = 2.0037$.

Synthesis of $Na(O_2CCH_2C_4H_3S)\cdot 6H_2O$. To a suspension of 3-thiopheneacetic acid (2000 mg, 14 mmol) in water, 50 mL of an aqueous solution of NaOH (560 mg, 14 mmol) was added. After 30 min of stirring, the resulting solution was filtered and the solvent was removed by rotary evaporation. The white solid obtained was washed several times with acetone and dried in air. Yield: 89%. Anal. Calcd for $C_6H_{17}O_8SNa$: C, 26.47; H, 6.29. Found: C, 27.13; H, 6.49. IR (KBr, cm^{-1}): ν(OH), 3386 (s, br); ν(CH), 3103 (m); $\nu(CH_2)$, 2908 (m); ν_{asym}(COO), 1560 (s); ν_{sym}(COO), 1391 (s); δ_{oop}(CH), 833 (s), 739 (s), 683 (s).

Synthesis of $[Cu_2\mu$-$(O_2CCH_2C_4H_3S)_4]$ (1). A 15 mL volume of an aqueous solution of $CuCl_2\cdot 2H_2O$ (170 mg, 1 mmol) was added dropwise under stirring to a solution of $Na(O_2CCH_2C_4H_3S)\cdot 6H_2O$ (545 mg, 2 mmol) in 20 mL of water at room temperature. The product precipitated immediately as a green solid and was filtered off, washed with cold water and acetone, and dried under vacuum. Yield: 87%. Mp: 215 °C (dec). Anal. Calcd for $C_{24}H_{20}O_8S_4Cu_2$: C, 41.67; H, 2.91; Cu, 18.37. Found: C, 40.97; H, 2.78; Cu, 19.22. IR (KBr, cm^{-1}): ν(CH), 3095 (m); $\nu(CH_2)$, 2920 (m); ν_{asym}(COO), 1589 (s); ν_{sym}(COO), 1410 (s); δ_{oop}(CH), 831 (s), 746 (s), 694 (s).

Synthesis of {$[Cu_2(O_2CCH_2C_4H_3S)_4\mu$-$(BPP)_2]$}$_n$ (2). A 20 mg (0.1 mmol) amount of the ligand BPP dissolved in 10 mL of ethanol was slowly added to 40 mL of a solution of $[Cu_2\mu$-$(O_2$-$CCH_2C_4H_3S)_4]$ **(1)** (70 mg, 0.1 mmol) in ethanol. The reaction mixture was kept under stirring at room temperature for 12 h, followed by reduction to one-fourth its original volume. The resulting light-blue powder was filtered off, washed with ethanol and acetone, and dried in air. Dark blue crystals suitable for X-ray analysis were grown after 4 weeks by slow evaporation of a DMSO solution. Yield: 60%. Mp: 160 °C (dec). Anal. Calcd for $C_{25}H_{24}N_2O_4S_2Cu$: C, 55.18; H, 4.45; N, 5.15; Cu, 11.68. Found: C, 56.30; H, 4.61; N, 5.20; Cu, 11.74. IR (KBr, cm^{-1}): ν(CH), 3078 (w), 3060 (w), 3044 (w); $\nu(CH_2)$, 2936 (w), 2863 (w); ν_{asym}(COO), 1603 (sh); ν(CC/CN), 1618 (vs), 1505 (m), 1430 (m); ν_{sym}(COO), 1368 (m), 1344 (m); δ_{oop}(CH), 840 (w), 759 (m), 687 (m). It should be noted that the light-blue powder presents the same analytical and spectroscopy data as the dark blue crystals. In addition, complex **2** can be prepared in one step by direct reaction of $CuCl_2\cdot 2H_2O$ and the sodium salt in the presence of BPP ligand. The yields are equivalent for both synthetic methods.

Table 1. Crystallographic Data and Structure Refinament Parameters for Compound **2**

chem formula	$C_{50}H_{48}Cu_2N_4O_8S_4$
fw	1088.24
cryst system	monoclinic
space group	$P2_1/c$
a/Å	9.4253(10)
b/Å	10.9373(10)
c/Å	23.6378(10)
β/deg	98.733(4)
V/Å^3	2408.5(4)
Z	2
D_{calcd}/g cm^{-3}	1.501
μ/cm^{-1}	11.15
final R value $[I > 2\sigma(I)]^a$	0.0386
$R_w{}^b$ (all data)	0.1280

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o{}^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

X-ray Data Collection and Structure Determination. Single-crystal X-ray diffraction measurement of complex **2** was carried out on an Enraf-Nonius CAD-4 diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 293(2) K. A total of 4380 reflections were collected in the $2.55 \leq \theta \geq 25.09$ range, of which 4269 were unique ($R_{int} = 0.0215$) and 2985 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS97[8] and refined by full-matrix least-squares procedure based on F^2 using SHELXL97 program.[9] Crystal data and structure refinement parameters are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. Compound **1** was prepared through reaction between $CuCl_2\cdot 2H_2O$ and the corresponding sodium salt of 3-thiopheneacetic acid, resulting in a typical dinuclear paddle-wheel structure. Reactivity studies of **1** toward the flexible nitrogen ligand BPP led to the formation of title complex **2**, in which the rupture of original lantern structure was observed. Previous reports reveal that in most cases the addition of different ligands L like DMSO,[6c,10] DMF,[6a,6d,11] CH_3CN,[12] pyridine,[5a,13] and 2-anilinopyridine[14] to dimeric tetracarboxylates allows the formation of discrete adducts generally formulated as $[Cu_2\mu$-$(O_2CR)_4(L)_2]$, where L is coordinated to apical positions. In other instance, polymeric structures can also be obtained by means of bifunctional ligands, which are able to axially

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(8) Sheldrick, G. M. *SHELXS97*, *Program for the solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(9) Sheldrick, G. M. *SHELXL97*, *Program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(10) Sapiña, F.; Burgos, M.; Escrivá, E.; Folgado, J.-V.; Beltrán, D.; Gómez-Romero, P. *Inorg. Chim. Acta* **1994**, *216*, 185−190.

(11) Morgant, G.; Dung, N.-H.; Daran, J.-C.; Viossat, B.; Labouze, X.; Roch-Arveiller, M.; Greenaway, F. T.; Cordes, W.; Sorenson, J. R. J. *J. Inorg. Biochem.* **2000**, *81*, 11−22.

(12) (a) Agterberg, F. P. W.; Provó Kluit, H. A. J.; Driessen, W. L.; Reedijk, J.; Oevering, H.; Buijs, W.; Veldman, N.; Lakin, M. T.; Spek, A. L. *Inorg. Chim. Acta* **1998**, *267*, 183−192. (b) Kögerler, P.; Williams, P. A. M.; Parajón-Costa, B. S.; Baran, E. J.; Lezama, L.; Rojo, T.; Müller, A. *Inorg. Chim. Acta* **1998**, *268*, 239−248.

(13) Morgan, Y. R.; Turner, P.; Kennedy, B. J.; Hambley, T. W.; Lay, P. A.; Biffin, J. R.; Regtop, H. L.; Warwick, B. *Inorg. Chim. Acta* **2001**, *324*, 150−161.

(14) Seco, J. M.; Garmendia, M. J. G.; Pinilla, E.; Torres, M. R. *Polyhedron* **2002**, *21*, 457−464.

connect dinuclear paddle-wheel units, as pyrazine,[15] 2-aminopyrimidine,[16] *N*,*N*′-hexamethylenetetramine,[17] and pyridyl nitronyl nitroxide.[18] In contrast, the current literature describes the formation of mononuclear Cu^{II} carboxylates from the reaction of dimeric tetracarboxylates with nitrogen or oxygen donor monofunctional ligands.[19] It has been recently reported an investigation of the critical role of counteranions in the construction of supramolecular arrays involving Cu^{II} acetate and Cu^{II} perchlorate with the angular dipyridyl ligand 2,5-bis(4-pyridyl)-1,3,4-oxadiazole.[20] Whereas an unprecedented Cu^{II} diamondoid net with 2-fold interpenetrating frameworks was obtained in the presence of ClO_4^- anions, the formation of an unexpected mononuclear complex with acetate anions was observed. In this case, the acetate anions as well as the nitrogen ligand coordinate to the Cu^{II} center in a monodentate fashion.

The most relevant aspect for the IR spectra of **1** and **2** is concerned with the values of asymmetric and symmetric stretching frequencies for COO^- groups. In this class of compounds, the difference between $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ ($\Delta\nu$) in comparison to the corresponding values in ionic species is currently employed to determine a characteristic coordination mode of carboxylate group.[21] For **1**, both absorption bands are shifted to higher frequencies relative to the sodium 3-thiopheneacetate. In addition, $\Delta\nu$ equal to 179 cm^{-1} is similar to that one observed for sodium salt, $\Delta\nu = 169$ cm^{-1}. These results indicate that the carboxylate groups in **1** coordinate to metal ions in a symmetrical bridging mode (*syn,syn*-η^1:η^1:μ_2) in agreement with the paddle-wheel type structure. On the other hand, it can be seen that, for compound **2**, the $\nu_{asym}(COO)$ band displays a blue shift, whereas two distinct $\nu_{sym}(COO)$ bands are shifted to lower frequencies from ionic values. The greater separations $\Delta\nu$ of 234 and 259 cm^{-1} respectively provide good evidence for the monodentate and monatomic bridging coordination modes of 3-thiopheneacetate to Cu^{II} sites in the title complex, which is consistent with the crystal structure, as described later. Besides these considerations, it should be noted that, in **2**, the pyridine ring vibrational band shifts from 1605 cm^{-1} in free BPP to 1618 cm^{-1}. In fact, the presence of ν(CC/CN) at a higher wavenumber is indicative of metal coordination[22a] to BPP pyridine nitrogens, as observed for previous structurally characterized compounds of formula $[M(BPP)_2(NO_3)_2]\cdot 2C_6H_6$, where M = Co and Cd.[22b]

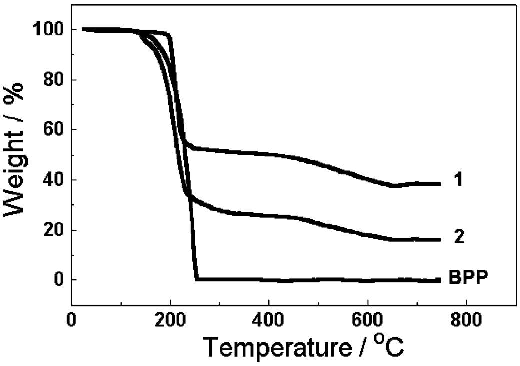

Figure 1. TG curves of $[Cu_2\mu\text{-}(O_2CCH_2C_4H_3S)_4]$ (**1**), $\{[Cu_2(O_2CCH_2C_4H_3S)_4\mu\text{-}(BPP)_2]\}_n$ (**2**), and BPP.

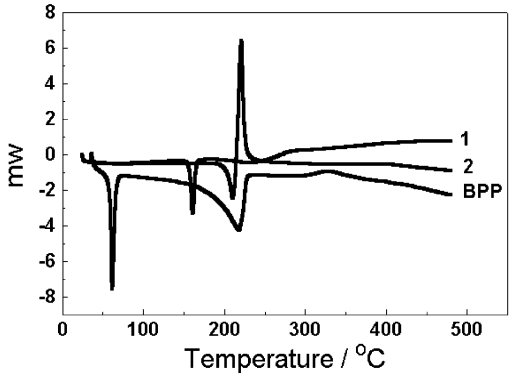

Figure 2. DSC curves of $[Cu_2\mu\text{-}(O_2CCH_2C_4H_3S)_4]$ (**1**), $\{[Cu_2(O_2CCH_2C_4H_3S)_4\mu\text{-}(BPP)_2]\}_n$ (**2**), and BPP.

The results of thermogravimetric analyses presented in Figure 1 show that there is no weight loss until 200 and 160 °C for **1** and **2**, respectively, indicating the absence of solvent molecules in both complexes. Above these temperatures can be observed the steps of their respective thermal decompositions. Noticeable, the initial decomposition temperature of **2** seems to be driven by the thermal stability of the BPP ligand. In addition, the residual percentage weight (obsd, 16.0%) at the end of the decomposition of **2** is consistent with the formation of CuO (calcd, 14.6%), in association with a black amorphous material which was supported by the X-ray powder diffraction pattern.

The DSC curves for **1**, **2**, and the BPP ligand are shown in Figure 2. For **1**, an endothermic peak at 210 °C can be observed immediately followed by an exothermic event at 221 °C corresponding to lantern breakdown. On the other hand, the DSC curve for **2** exhibits a completely distinct pattern and shows clearly the absence of the BPP melting peak at 61 °C.

Description of the Crystal Structure of 2. The polymeric nature of **2** was revealed by X-ray single-crystal structure analysis. Figure 3 shows the first Cu^{II} coordination sphere in a distorted square planar geometry. A Cu^{II} ion is coordinated by two carboxylate oxygen atoms of distinct 3-thiopheneacetate groups as well as two pyridyl nitrogen atoms from different BPP ligands in a trans arrangement. Selected bond distances and angles in close agreement with

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(15) Takamizawa, S.; Nakata, E.; Yokoyama, H. *Inorg. Chem. Commun.* **2003**, *6*, 763−765.

(16) Smith, G.; Kennard, C. H. L.; Byriel, K. A. *Polyhedron* **1991**, *10*, 873−876.

(17) Pickardt, J. *Acta Crystallogr.* **1981**, *B37*, 1753−1756.

(18) Chung, Y.-H.; Wei, H.-H. *Inorg. Chem. Commun.* **1999**, *2*, 269−271.

(19) (a) Heimer, N. E.; Ahmed, I. Y. *Inorg. Chim. Acta* **1982**, *64*, L65−L66. (b) Bhirud, R. G.; Srivastava, T. S. *Inorg. Chim. Acta* **1990**, *173*, 121−125. (c) Abuhijleh, A. L.; Woods, C.; Ahmed, I. Y. *Inorg. Chim. Acta* **1991**, *190*, 11−17. (d) Petric, M.; Leban, I.; Segedin, P. *Polyhedron* **1996**, *15*, 4277−4282. (e) Moncol, J.; Palicová, M.; Segl'a, P.; Koman, M.; Melník, M.; Valko, M.; Glowiak, T. *Polyhedron* **2002**, *21*, 365−370.

(20) Du, M.; Bu, X.-H.; Guo, Y.-M.; Liu, H.; Batten, S. R.; Ribas, J.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 4904−4908.

(21) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227−250. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(22) (a) Scopelliti, R.; Bruno, G.; Donato, C.; Tresoldi, G. *Inorg. Chim. Acta* **2001**, *313*, 43−55. (b) Bujaci, M. T.; Wang, X.; Li, S.; Zheng, C. *Inorg. Chim. Acta* **2002**, *333*, 152−154.

$\{[Cu_2(O_2CCH_2C_4H_3S)_4\mu\text{-}(BPP)_2]\}_n$

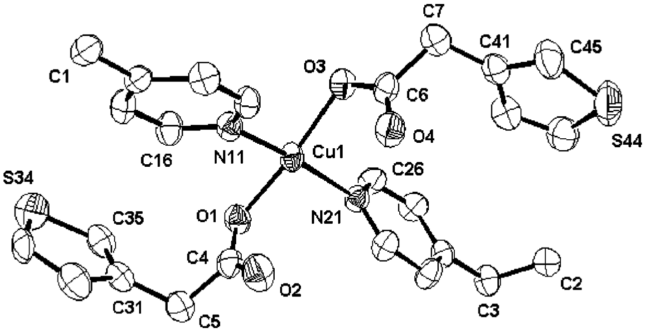

Figure 3. ORTEP[23] drawing of the first coordination sphere of Cu^{II} ion in the asymmetric unit of **2** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

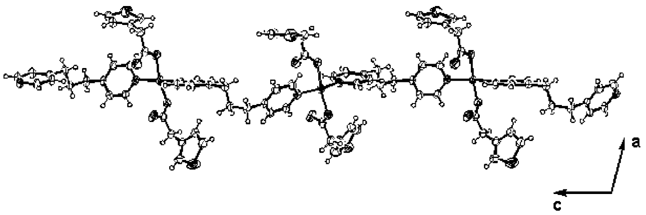

Figure 4. View of the 1-D sinusoidal polymeric chain in compound **2** along the crystallographic *b* axis.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

Cu(1)−O(1)	1.953(2)	C(4)−O(1)	1.270(4)
Cu(1)−O(3)	1.990(2)	C(4)−O(2)	1.238(4)
Cu(1)−N(11)	2.027(3)	C(6)−O(3)	1.291(4)
Cu(1)−N(21)	2.015(3)	C(6)−O(4)	1.214(4)
O(1)−Cu(1)−O(3)	166.77(10)	O(1)−Cu(1)−N(21)	89.42(10)
N(11)−Cu(1)−N(21)	165.53(11)	O(3)−Cu(1)−N(11)	93.13(10)
O(1)−Cu(1)−N(11)	90.11(10)	O(3)−Cu(1)−N(21)	90.62(10)

previous reported for Cu^{II} carboxylates containing nitrogen aromatic heterocyclic ligands are given in Table 2.[19a,20]

The BPP ligands connect the Cu^{II} centers resulting in a neutral one-dimensional polymeric chain propagated in direction of the crystallographic *c* axis as depicted in Figure 4. As can be seen, each BPP molecule adopts a TG conformation, in which the N-to-N distance is 8.894(4) Å. The 1-D sinusoidal chain presents a period equivalent to the unit cell length *c* of 23.64 Å. In addition, the shortest intrachain Cu···Cu separation is 12.1689(5) Å.

Studies on coordination polymers constructed through the interaction of metal cations with the flexible ligand BPP have been reported.[4] Among these several known coordination polymers, sinusoidal chains similar to **2** have been found in $[Ag(BPP)]NO_3$,[4b] $[Ag(BPP)](CF_3SO_3)\cdot EtOH$,[4a] [Ag(BPP)]X ($X = ClO_4^-$, PF_6^-),[4i] and $[Cu(BPP)]BF_4$.[4l] The former silver polymer is the only one that presents the BPP ligand in a TG conformation with N-to-N distance of 8.79 Å and repeat length of 23.98 Å. In all other structures, BPP displays a TT conformation providing larger N-to-N separations and consequently higher periodic wavelengths.

The most prominent structural feature of **2** is that each adjacent 1-D sinusoidal chain is cross-linked by monatomic oxygen bridges increasing the polymeric dimensionality along the crystallographic *b* axis to form a 2-D network. As conveniently shown in Figure 5, the carboxylate ligands exhibit distinct coordination behavior. Two 3-thiopheneacetate groups act as monodentate whereas the remaining two adopt a monatomic bridging mode (μ-oxo) resulting in a centrosymmetric dimeric unit Cu_2O_2. The presence of both monodentate and monatomic bridging modes in the coordination environment of each Cu^{II} center is relatively rare, and some examples structurally characterized have been found in the literature.[7b]

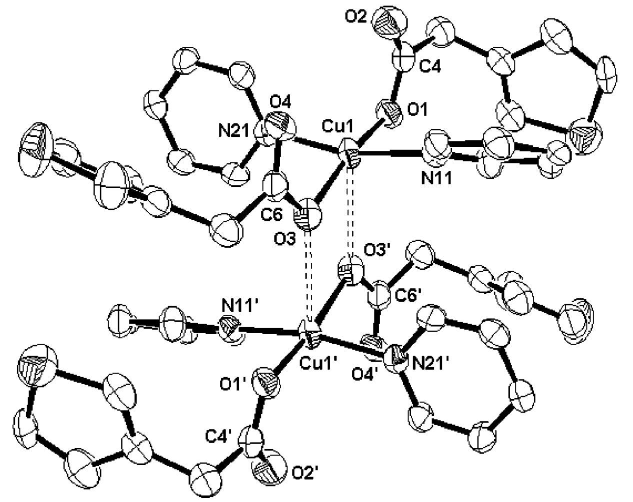

Figure 5. ORTEP[23] view of the dimeric unit (Cu_2O_2) in **2** showing the formation of the monoatomic carboxylate bridges with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; atoms marked with a prime (′) are at the symmetry position $-x$, $-y$, $-z$.

It is interesting to note that the Cu_2O_2 motif is strictly planar and each bridging oxygen involving in the chain extension (O3′ and O3) simultaneously occupies an apical site at one Cu^{II} ion and the basal position of the other Cu^{II} cation, resulting in a markedly longer Cu1−O3′ distance [2.695(3) Å] than the bond length Cu1−O3 [1.990(2) Å]. This is a typical structural aspect for parallel-planar dinuclear Cu^{II} complexes with two monatomic bridging carboxylates[7b] and can be attributed to the Jahn−Teller effect. The Cu1···Cu1′ separation is 3.895(1) Å and the bridging angle φ(Cu−O−Cu) is 111.62(10)°, which are higher when compared with related compounds containing monatomic bridging carboxylates,[7] probably because of steric requirements in the solid state. The coordination number around the copper(II) ions is 4 + 1 due to CuO_2N_2O' cromophore, and the geometry is best described as a square pyramid with a trigonality index $\tau = 0.02$ ($\tau = \beta - \alpha/60$, where β is the greatest basal angle and α is the second in magnitude; $\tau =$ 0 and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries, respectively).[24] A drawing of the two-dimensional network of **2** viewed along the *a* direction is presented in Figure 6.

The topology of the 2-D network is of the (6,3) type and can be described as a wavelike brick wall. In fact, the known $[Ag(BPP)]PF_6$[4i] and $[Cu(BPP)]BF_4$[4l] display extended supramolecular structures similar to that of **2**; however, in those cases the interchain interactions occurs by metal−metal

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(23) Farrugia, L. J. ORTEP-3 for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(24) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

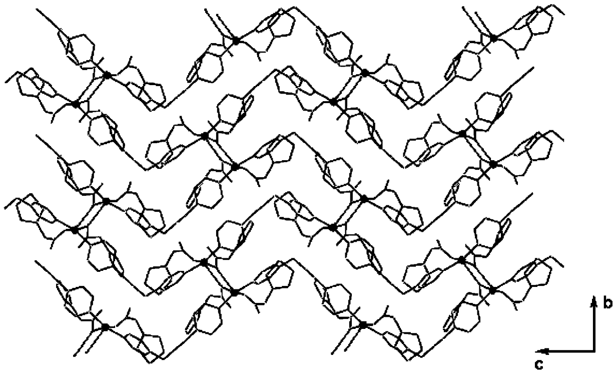

Figure 6. Perspective view of the extended 2-D coordination network in **2** along the crystallographic *a* axis.

contacts. To the best of our knowledge **2** is the first example of Cu^{II} coordination polymer containing a nitrogen bidentate donor ligand and carboxylate groups in which the 1-D chains extend into a 2-D network through monatomic oxygen bridges.

Electron Paramagnetic Resonance Spectra. The powder EPR spectrum of **1** at room temperature shows only a very broad line (600 G) with strongly reduced intensity and without any fine structure. In fact, this behavior is commonly observed in anhydrous or nonadduct paddle-wheel type copper(II) carboxylates $[Cu_2\mu\text{-}(O_2CR)_4]$, due to strong antiferromagnetic coupling between the two Cu^{II} ions. In this case, the metal centers are interconnected with distance in the range of (2.58−2.89 Å) and the spin interaction occurs through conjugated π-system of carboxylate bridges.[5b,25]

The polycrystalline EPR spectrum of **2** measured at room temperature is shown in Figure 7. It exhibits broad features characteristic of a triplet spin state with a nonnegligible zero-field splitting, due to the coupling of the two $S = 1/2$ spins within a dinuclear unit. At low temperature (~50 K) the same X-band EPR spectral pattern was observed. In addition, another confirmation that we are dealing with two magnetically coupled Cu^{II} ions with an effective spin $S = 1$ comes from the observation of the half-field transition at about 1.6 kG.

The EPR spectra have been analyzed using the following spin Hamiltonian[26] in a least-squares fit routine:

$$H = \beta \mathbf{B} g \mathbf{S} + D[S_z^{\,2} - 2/3] + E[S_x^{\,2} - S_y^{\,2}]$$

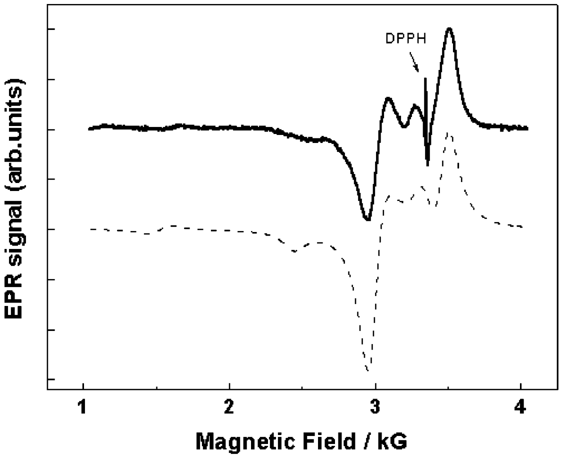

Figure 7. Polycrystalline EPR spectrum at room temperature for **2** (solid line). The best simulation is shown as a dashed line.

The two terms correspond to the electron Zeeman and the fine structure interaction, respectively.

The experimental spectrum was well reproduced using the parameters in an axial symmetry of $g_{\|} = 2.33$, $g_{\perp} = 2.07$, $D = 0.05\ \text{cm}^{-1}$, and $E = 0\ \text{cm}^{-1}$, as can be seen in Figure 7. The average g value can be calculated according to $\bar{g} = (1/3)(g_{\|} + 2g_{\perp})$, which result in $\bar{g} = 2.16$. These results are consistent taking into account the crystal structure of compound **2**, in which the Cu···Cu separations across the 1-D sinusoidal chain are very large and no significant magnetic interaction can be expected. However, considering two neighboring chains and the presence of the dimeric unit Cu_2O_2 within the 2-D network, the distance between two Cu^{II} ions is about 3.9 Å. In this situation EPR spectra of two coupled Cu^{II} ions in a square-pyramidal CuO_2N_2O' environment with a basically $d_{x^2-y^2}$ ground state can be observed, in agreement with the literature for similar μ-oxo carboxylate-bridged copper(II) dimers.[7]

Conclusion

In summary, this study provides an interesting example of a Cu^{II} coordination polymer constructed from the flexible nitrogen ligand BPP and the carboxylate anion 3-thiopheneacetate. In this case, the 1-D sinusoidal chains extend into a 2-D network due to the ability of Cu^{II} ion to assume five-coordination geometry and adoption of the monatomic bridging mode by the carboxylate group.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) (a) Agterberg, F. P. W.; Kluit, H. A. J. P.; Driessen, W. L.; Oevering, H.; Buijs, W.; Lakin, M. T.; Spek A. L.; Reeddijk, J. *Inorg. Chem.* **1997**, *36*, 4321−4328. (b) Doyle, A.; Felcman, J.; Gambardella, M. T. P.; Verani, C. N.; Tristão, M. L. B. *Polyhedron* **2000**, *19*, 2621−2627.

(26) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173−278.