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Inorganic Chemistry Article

Synthesis and Characterization of Novel Dinuclear Copper(I) Complexes. Dimerization of [CuL(PPh_3)$_2$] (L = methyl 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioate)

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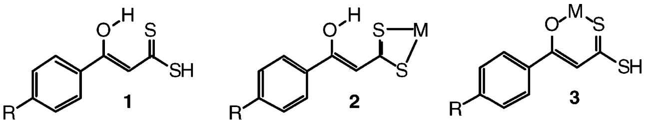
We report the synthesis of new copper(I) complexes **6a**–**e** from methyl 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioate ligands. These complexes were characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The expected O,S-coordination mode was confirmed by the X-ray diffraction studies of **6b** and **6e**. The unexpected dimerization of **6b**–**e** leads to the formation of four novel dinuclear copper(I) compounds (**7b**–**e**). The dinuclear complex structure was fully established by the X-ray diffraction analysis of **7a**, in which the presence of a Cu–Cu interaction was observed.

Introduction

The organosulfur compounds are useful ligands, and their metal complexes have been applied as catalysts in a variety of reactions such as hydrosilylation, oxygen activation, ethylene oligomerization, enantioselective Diels Alder, and asymmetric epoxidation, among others.[1] Although the 3-hydroxy-3-(*p*-R-phenyl)-2-propendithioic acids (**1**) have been known since 1888,[2] they have rarely been used as ligands.[3] Two coordination modes have been proposed for these compounds,[3a,4] taking into account the structural arrangement of donor atoms (Chart 1): (a) an S,S-coordination mode, forming a four-membered chelated ring (**2**) and (b) an O,S-coordination mode, forming a six-membered chelated ring (**3**); only the former has been observed.

Chart 1. Proposed Coordination Fashion of Compound **1**



Recently, we have shown that the S,S-coordination mode is preferred over the O,S-mode in 3-hydroxy-3-(*p*-R-phenyl)-2-propendithioic acids **1**, and this behavior could be explained by electronic correlation analysis.[5] Furthermore, these copper(I) coordination compounds (**4**) display a tautomeric equilibrium in solution (Chart 2).

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(1) Among others: (a) Evans, D. A.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534. (b) Mandimutsira, B. S.; Yamarik, J. L.; Brunold, T. C.; Gu, W.; Cramer, S. P.; Riordan, C. G. *J. Am. Chem. Soc.* **2001**, *123*, 9194. (c) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (d) Smith, J. N.; Shirin, Z.; Carrano, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 868. (e) Mancheno, O. G.; Arrayas, R. G.; Carretero, J. C. *Organometallics* **2005**, *24*, 557. (f) Xia, Q.-H.; Ge, H.-Q.; Ye, C.-P.; Liu, Z.-M.; Su, K.-X. *Chem. Rev.* **2005**, *105*, 1603.

(2) (a) Meyer, V. *Ber.* **1888**, *21*, 353. (b) Kelver, C. *Ber.* **1910**, *43*, 1252. (c) Kelver, C.; Schwars, A. *Ber.* **1911**, *44*, 1698. (d) Kelver, C.; Schwars, A. *Ber.* **1912**, *45*, 137.

(3) (a) Weignad, W.; Bosl, K.; Polborn, K. *Chem. Ber.* **1990**, *123*, 1339. (b) Weigand, W.; Saumweber, R.; Schulz, P. *Z. Naturforsch.* **1993**, *48b*, 1080. (c) Buchweitz, J.; Gompper, R.; Polborn, K.; Robl, C.; Sailer, M.-T.; Weigand, W. *Chem. Ber.* **1994**, *127*, 23. (d) Alvarez-Toledano, C.; Enríquez, J.; Alfredo Toscano, R.; Martínez-García, M.; Cortés-Cortés, E.; Osornio, Y. M.; García-Mellado, O.; Gutiérrez-Pérez, R. *J. Organomet. Chem.* **1999**, *38*, 577. (e) Alvarez-Toledano, C.; Delgado, E.; Donnadieu, B.; Hernández, E.; Martín, G.; Zamora, F. *Inorg. Chim. Acta* **2003**, *351*, 119.

(4) (a) Coucouvanis, D.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 1346. (b) Caffery, M. L.; Coucouvanis, D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2081. (c) Liu, C.-Y.; Lih, J.-J. *Fresenius' J. Anal. Chem.* **1988**, *332*, 171.

(5) García-Orozco, I.; López-Cortés, J. G.; Alfredo Toscano, R.; Penieres Carrillo, G.; Alvarez-Toledano, C. *Inorg. Chem.* **2004**, *43*, 8572.

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Chart 2. Tautomeric Equilibrium of Copper(I) Complexes from Ligands **1**

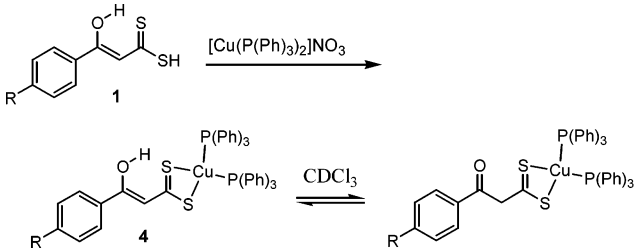
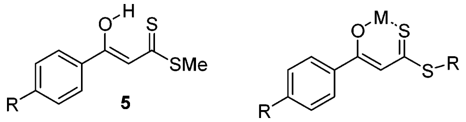


Chart 3. Observed Coordination Mode of Compound **5**



To study the less favored O,S-coordination of dithio acids **1**, we could possibly use dithioester derivatives[6] (**5**), taking advantage of the minor coordination capability of the −SMe rather than the −SH group.[7] These compounds have received more attention as ligands[8] than dithio acids **1**, because of their stability and the monothio-β-diketone similarity (Chart 3). Nickel (II),[8c] copper(II),[8a,d] cobalt(III), and zinc(II)[8d] complexes of dithioester derivatives have been obtained that show electron delocalization over the six-membered chelated ring.[8d] Furthermore, manganese(II), iron(II), cobalt(II and III), nickel(II), palladium(II), platinum(II), copper(II), and zinc(II) complexes of these ligands with large chain substituents were synthesized for possible use as metallomesogenes.[8e] In all cases, the dithioester derivatives display an O,S-coordination mode, forming a six-membered chelated ring.

With the aim of continuing our studies about the reactivity of type **1** ligands toward transition metals, we studied the copper(I) O,S-coordination mode in the corresponding dithioester compound **5.** In this paper, we report the synthesis and structural characterization of new copper(I) complexes of 3-hydroxy-3-(*p*-R-phenyl)-2-propendithioic methyl esters and their unexpected dimerization to obtain novel dinuclear copper(I) complexes.

Experimental Section

Materials. Infrared spectra were recorded on either a Perkin-Elmer 283B or 1420 spectrophotometer, and data are expressed in wavenumbers (cm^{-1}). All NMR spectra were recorded on a JEOL Eclipse +300 using $CDCl_3$ as the solvent, and the chemical shifts were referenced to TMS in ^{1}H and ^{13}C and 30% H_3PO_4 in ^{31}P. The MS−FAB spectra were obtained on a JEOL JMS SX 102A. Elemental analyses were performed by the USAI, Facultad de Química UNAM. Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. All commercial reagents were of ACS grade and used without further purification. THF was distilled from benzophenone under nitrogen atmosphere. The 3-hydroxy-3(*p*-R-phenyl)propendithioic acids **1** were synthesized according to Larsson's method.[6a] Bis(triphenylphosphine)copper(I) nitrate was obtained by previous literature preparation.[9]

General Procedure. Synthesis of Methyl 3-Hydroxy-3-(*p*-methoxyphenyl)-2-propenedithioate (5a). To a solution of 3-hydroxy-3-(*p*-metoxyphenyl)-2-propendithioic acid (1.11 g, 4.8 mmol) in 15 mL of THF were added calcium hydride (0.10 g, 2.4 mmol) and methyl iodide (0.3 mL, 4.8 mmol) at room temperature. The mixture was stirred for 2 h and then extracted with water and ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo. The product was purified by silica gel (70−230 mesh) chromatography using hexane as the eluant to obtain a crystalline yellow solid. Yield: 0.10 g (8%). Mp: 76−77 °C. IR (KBr, cm^{-1}): 3430.5 w, 1603.1 m, 1582.0 s, 1545.9 m, 1503.9 s, 1430.2 m, 1232.3 s, 1180.9 m, 1052.8 m, 959.6 m, 838.2 m, 782.2 m, 585.1 m, 454.6 m. MS-EI+ (*m*/*z* %): 240 (M$^+$, 51), 193 ([M − MeS]$^+$, 100), 135 ([$MeOC_6H_4CO$]$^+$, 86.2), 107 ([$MeOC_6H_4$]$^+$, 6.88). ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 3H, H-8), 3.87 (s, 3H, MeO), 6.95 (d, 2H, J = 8.70 Hz, H-6), 6.95 (s, 1H, H-2), 7.86 (d, 2H, J = 8.70 Hz, H-5), 15.19 (s, 1H, H-9). ^{13}C NMR ($CDCl_3$): δ 17.0 (C-8), 55.6 (MeO), 107.2 (C-2), 114.3 (C-6), 126.3 (C-4), 128.7 (C-5), 162.9 (C-7), 169.6 (C-3), 215.7 (C-1).

Synthesis of Methyl 3-Hydroxy-3-(*p*-methylphenyl)-2-propenedithioate (5b). Yield: 0.84 g (79%). Mp: 58−60 °C. IR (KBr, cm^{-1}): 3382.6 w, 1654 w, 1584.0 s, 1560.3 s, 1529.8 m, 1502.9 s, 1456.8 m, 1421.3 m, 1236.9 s, 1184.9 m, 1051.5 m, 943.2 m, 833.4 m, 771.4 m, 673.1 m, 567.9 m, 547.6. MS-EI+ (*m*/*z* %): 224 (M$^+$, 63), 177 ([M − MeS]$^+$, 100), 119 ([MeC_6H_4CO]$^+$, 62), 91 ([MeC_6H_4]$^+$, 42). ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H, Me), 2.67 (s, 3H, H-8), 6.97 (s, 1H, H-2), 7.25 (d, 2H, J = 8.49 Hz, H-6), 7.79 (d, 2H, J = 8.49 Hz), 15.13 (s, 1H, H-9). ^{13}C NMR ($CDCl_3$): δ 17.1 (C-8), 21.7 (Me), 107.6 (C-2), 126.8 (C-6), 129.6 (C-5), 131.4 (C-4), 142.8 (C-7), 169.7 (C-3), 216.7 (C-1).

Synthesis of Methyl 3-Hydroxy-3-phenyl-2-propenedithioate (5c). Yield: 0.65 g (52%). Mp: 55−57 °C. IR (KBr, cm^{-1}): 3731.9 w, 1585.7 m, 1559.0 s, 1489.3 m, 1451.6 m, 1392.1 m, 1298.5 w, 1236.3 s, 1055.7 m, 961.2 m, 938.9 s, 823.0 m, 754.2 s, 682.9 m, 605.5 m, 547.9 m. MS-EI+ (*m*/*z* %): 210 (M$^+$, 53), 163 ([M − MeS]$^+$, 100), 105 ([C_6H_5CO]$^+$, 61), 77 ([C_6H_5]$^+$, 41). ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 3H, H-8), 6.96 (s, 1H, H-2), 7.46 (m, 1H, H-7), 7.47 (m, 2H, H-6), 7.88 (m, 2H, H-5), 15.09 (s, 1H, H-9). ^{13}C NMR ($CDCl_3$): δ 17.2 (C-8), 107.9 (C-2), 126.8 (C-6), 128.8 (C-5), 131.9 (C-7), 134.3 (C-4), 169.3 (C-3), 217.4 (C-1).

Synthesis of Methyl 3-Hydroxy-3-(*p*-fluorophenyl)-2-propenedithioate (5d). Yield: 0.76 g (71%). Mp: 94−96 °C. IR (KBr, cm^{-1}): 3432.0 w, 1600.4 s, 1575.0 s, 1501.3 s, 1426.5 m, 1226.1 s, 1162.6 m, 1053.6 m, 963.1 m, 844.7 m, 763.3 m, 573.0 m, 545.9 m, 467.0 m. MS-EI+ (*m*/*z* %): 228 (M$^+$, 61), 181 ([M − MeS]$^+$, 100), 123 ([FC_6H_4CO]$^+$, 61), 95 ([FC_6H_4]$^+$, 27). ^{1}H NMR ($CDCl_3$): δ 2.66 (s, 3H, H-8), 6.90 (s, 2H, H-2), 7.14 (m, 2H, H-6), 7.90 (m, 2H, H-5), 15.11 (s, 1H, H-9). ^{13}C NMR ($CDCl_3$): δ 17.2 (C-8), 107.6 (C-2), 116.0 (d, $^2J_{C-F}$ = 21.9 Hz, C-6), 129.0 (d, $^3J_{C-F}$ = 8.6 Hz, C-5), 130.5 (C-4), 165.0 (d, $^1J_{C-F}$ = 253.8 Hz, C-7), 168.1 (C-3), 217.9 (C-1).

Synthesis of Methyl 3-Hydroxy-3-(*p*-chlorophenyl)-2-propenedithioate (5e). Yield: 0.33 g (31%). Mp: 76−77 °C. IR (KBr, cm^{-1}): 3429.4 w, 2922.1 w, 1591.0 s, 1555.5 m, 1485.2 m, 1415.6 m, 1229.9 m, 1092.0 m, 1054.0 m, 101.6 m, 962.5 m, 832.2 m, 778.5 m, 551.9 w, 439.2 w. MS-EI+ (*m*/*z* %): 244 (M$^+$, 52), 197

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[6] (a) Larsson, F. C. V.; Lawesson, S.-O. *Tetrahedron* **1972**, *28*, 5341. (b) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029.

[7] Murray, S. G.; Hartley, F. *Chem. Rev.* **1981**, *81*, 365.

[8] (a) Gompper, R.; Schaefer, H. *Chem. Ber.* **1967**, *100*, 591. (b) Dorange, G.; Schaefer, H. *Chem. Ber.* **1967**, *100*, 591. (c) Dorange, G.; Kergoat, R.; Guerchais, J. E. *Bull. Soc. Chim. Fr.* **1969**, 3835. (d) Dorange, G.; Guerchais, J. E. *Bull. Soc. Chim. Fr.* **1971**, 43. (e) Saumweber, R.; Robl, C.; Weignad, W. *Inorg. Chim. Acta* **1998**, *269*, 83.

[9] (a) Cotton, F. A.; Goodgame, D. M. L. *J. Chem. Soc.* **1960**, 5267. (b) Jardine, F. H.; Vohra, A. G.; Young, F. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2941.

([M − MeS]$^+$, 100), 139 ([ClC$_6$H$_4$CO]$^+$, 63), 111 ([ClC$_6$H$_4$]$^+$, 26). ^{1}H NMR (CDCl$_3$): δ 2.66 (s, 3H, H-8), 6.91 (s, 1H, H-2), 7.42 (d, 2H, J = 8.95 Hz, H-6), 7.82 (d, 2H, J = 8.95 Hz, H-5), 15.06 (s, 1H, H-9). ^{13}C NMR (CDCl$_3$): δ 17.3 (C-8), 107.7 (C-2), 128.0 (C-6), 129.1 (C-5), 132.8 (C-4), 138.1 (C-7), 167.8 (C-3), 217.7 (C-1).

General Procedure for the Synthesis of Bis(triphenylphosphine-P)[methyl-3-hydroxy-3-(*p*-methoxy-phenyl)-2-propenedithioate-O,S]copper(I) (6a). To an aqueous solution of methyl-3-hydroxy-3(*p*-methoxy-phenyl)-propendithioate **5a** (0.10 g, 0.42 mmol) was added 2 mL of a 0.10 g/mL solution of NaOH (0.42 mmol) in ethanol and a solution of Cu(PPh$_3$)$_2$NO$_3$ (0.28 g, 0.42 mmol) in CH$_2$Cl$_2$. The orange solution turned dark red. The mixture was stirred for 15 min; the organic layer was then separated and dried with anhydrous Na$_2$SO$_4$. The solvent was distilled off under vacuum until there was a minimal amount of CH$_2$Cl$_2$; ethanol was then added to precipitate the complex, which was filtered and dried in a vacuum to give an orange solid. Yield: 0.21 g (60%). Mp: 148−150 °C. IR (KBr, cm^{-1}): 3430.0 w, 3050.9 w, 1602.1 m, 1582.9 m, 1537.4 m, 1442.5 vs, 1404.8 s, 1298.5 m, 1239.6 s, 1170.4 m, 1094.3 m, 1029.2 m, 934.9 m, 779.0 m, 744.3 m, 696.4 s, 509.8 m. FAB-MS+ (*m*/*z* %): 891 ([M + Cu]$^+$, 30). ^{1}H NMR (CDCl$_3$): δ 2.53 (s, 3H, H-8), 3.82 (s, 3H, MeO), 6.94 (s, 1H, H-2), 6.82 (d, 2H, J = 8.81 Hz, H-6), 7.71 (d, 2H, J = 8.81 Hz, H-5), 7.30 (m, 30H, PPh$_3$). ^{13}C NMR (CDCl$_3$): δ 17.0 (C-8), 55.4 (MeO), 110.2 (C-2), 113.3 (C-6), 128.5 (d, $^3J_{PC}$ = 8.6 Hz, C-*m*, PPh$_3$), 129.3 (C-5 + C-*p*, PPh$_3$), 133.9 (d, $^2J_{PC}$ = 15.5 Hz, C-*o*, PPh$_3$), 134.4 (d, $^1J_{PC}$ = 21.2 Hz, C-*ipso*, PPh$_3$), 134.8 (C-4), 161.6 (C-1), 181.4 (C-3), 188.2 (C-1). ^{31}P NMR (CDCl$_3$): δ-2.07 (broad signal). Anal. Calcd for C$_{47}$H$_{41}$CuO$_2$P$_2$S$_2$: C, 68.22; H, 4.99. Found: C, 69.29; H, 4.86.

Synthesis of Bis(triphenylphosphine-P)[methyl-3-hydroxy-3-(*p*-methyl-phenyl)-2-propenedithioate-O,S]copper(I) (6b). Yield: 0.29 g (85%). Mp: 152−154 °C. IR (KBr, cm^{-1}): 3382.6 w, 3050.9 w, 1581.9 m, 1532.8 m, 1441.4 s, 1398.8 m, 1316.9 m, 1292.0 m, 1241.9 m, 1181.9 m, 1094.0 m, 936.9 m, 777.2 m, 744.5 m, 695.7 s, 509.7 m. FAB-MS+ (*m*/*z* %): 875 ([M + Cu]$^+$, 52). ^{1}H NMR (CDCl$_3$): δ 2.36 (s, 3H, Me), 2.56 (s, 3H, H-8), 7.03 (s, 1H, H-2), 7.15 (d, 2H, J = 8.13 Hz, H-6), 7.68 (d, 2H, J = 8.13 Hz, H-5), 7.30 (m, 30H, PPh$_3$). ^{13}C NMR (CDCl$_3$): δ 17.0 (C-8), 21.6 (Me), 110.5 (C-2), 127.5 (C-6), 128.5 (d, $^3J_{PC}$ = 8.6 Hz, *C-m*, PPh$_3$), 128.8 (C-5), 129.4 (C-*p*, PPh$_3$), 133.9 (d, $^2J_{PC}$ = 16.6 Hz, C-*o*, PPh$_3$), 134.5 (d, $^1J_{PC}$ = 18.9 Hz, C-*ipso*, PPh$_3$), 139.3 (C-4), 140.8 (C-1), 182.2 (C-3), 189.3 (C-1). ^{31}P NMR (CDCl$_3$): δ −1.35 (broad signal). Anal. Calcd for C$_{47}$H$_{41}$CuOP$_2$S$_2$: C, 69.57; H, 5.09. Found: C, 70.16; H, 4.98.

Synthesis of Bis(triphenylphosphine-P)[methyl-3-hydroxy-3-phenyl-2-propenedithioate-O,S]copper(I) (6c). Yield: 0.17 g (43%). Mp: 172−175 °C. IR (KBr, cm^{-1}): 3427.2 w, 3052.0 w, 1585.8 w, 1534.6 m, 1456.6 s, 1428.7 s, 1314.8 m, 1290.9 m, 1238.7 m, 1094.5 m, 937.5 m, 806.6 m, 744.8 s, 695.0 s, 621.9 m, 508.6 s. FAB-MS+ (*m*/*z* %): 869 ([M + Cu]$^+$, 21) ^{1}H NMR (CDCl$_3$): δ 2.53 (s, 3H, H-8), 6.93 (s, 1H, H-2), 7.64 (m, 2H, H-5), 7.30 (m, 33H, PPh$_3$ + H-7 + H-6). ^{13}C NMR (CDCl$_3$): δ 17.0 (C-8), 110.5 (C-2), 127.3 (C-6), 128.4 (d, $^3J_{PC}$ = 8.7 Hz, *C-m*, PPh$_3$), 128.9 (C-5), 129.4 (C-*p*, PPh$_3$), 133.9 (d, $^2J_{PC}$ = 15.6 Hz, C-*o*, PPh$_3$), 134.6 (d, $^1J_{PC}$ = 19.6 Hz, C-*ipso*, PPh$_3$), 130.2 (C-4), 142.0 (C-1), 182.1 (C-3), 190.1 (C-1). ^{31}P NMR (CDCl$_3$): δ −2.22 (broad signal). Anal. Calcd for C$_{46}$H$_{39}$CuOP$_2$S$_2$: C, 69.28; H, 4.93. Found: C, 72.09; H, 4.90.

Synthesis of Bis(triphenylphosphine-P)[methyl-3-hydroxy-3-(*p*-fluoro-phenyl)-2-propenedithioate-O,S]copper(I) (6d). Yield: 0.24 g (62%). Mp: 163−164 °C. IR (KBr, cm^{-1}): 3430.8 w, 3051.9 w, 1598.0 m, 1530.0 m, 1477.3 m, 1443.8 s, 1397.0 m, 1309.7 m, 1230.3 m, 1154.1 m, 1093.9 m, 937.7 m, 847.9 m, 786.8 m, 744.7 m, 695.4 s, 597.7 m, 506.8 m. FAB-MS+)*m*/*z* %): 891 ([M + Cu]$^+$, 30). ^{1}H NMR (CDCl$_3$): δ 2.52 (s, 3H, H-8), 6.85 (s, 1H, H-2), 6.95 (m, 2H, H-6), 7.64 (m, 2H, H-5), 7.30 (m, 30H, PPh$_3$). ^{13}C NMR (CDCl$_3$): δ 16.9 (C-8), 110.4 (C-2), 115.1 (d, $^2J_{FC}$ = 21.2 Hz, *C*-6), 128.4 (d, $^3J_{PC}$ = 6.9 Hz, *C-m*, PPh$_3$), 129.4 (d, $^3J_{FC}$ = 13.7, C-5), 129.3 (C-*p*, PPh$_3$), 133.9 (d, $^2J_{PC}$ = 16.0 Hz, C-*o*, PPh$_3$), 134.2 (d, $^1J_{PC}$ = 32.9 Hz, C-*ipso*, PPh$_3$), 138.5 (C-4), 164.4 (C-1), 180.6 (C-3), 191.0 (C-1). ^{31}P NMR (CDCl$_3$): δ −2.26 (broad signal). Anal. Calcd for C$_{46}$H$_{38}$CuFOP$_2$S$_2$: C, 67.76; H, 4.70. Found: C, 67.53; H, 4.54.

Synthesis of Bis(triphenylphosphine-P)[methyl-3-hydroxy-3-(*p*-chloro-phenyl)-2-propenedithioate-O,S]copper(I) (6e). Yield: 0.26 g (75%). Mp: 143−144 °C. IR (KBr, cm^{-1}): 3443.0 w, 3376.9 w, 3051.7 w, 1581.5 m, 1528.0 m, 1442.3 s, 1312.5 m, 1285.8 m, 1092.1 m, 938.5 m, 744.0 m, 696.3 m, 509.4 m. FAB-MS+ (*m*/*z* %): 891 ([M + Cu]$^+$, 30) ^{1}H NMR (CDCl$_3$): δ 2.56 (s, 3H, H-8), 6.97 (s, 1H, H-2), 7.30 (d, 2H, J = 8.53 Hz, H-6), 7.67 (d, 2H, J = 8.53 Hz, H-5), 7.30 (m, 30H, PPh$_3$). ^{13}C NMR (CDCl$_3$): δ 16.9 (C-8), 110.1 (C-2), 128.5 (C-6), 128.4 (d, $^3J_{PC}$ = 9.2 Hz, *C-m*, PPh$_3$), 128.7 (C-5), 129.4 (C-*p*, PPh$_3$), 134.0 (d, $^2J_{PC}$ = 16.1 Hz, C-*o*, PPh$_3$), 134.3 (d, $^1J_{PC}$ = 20.6 Hz, C-*ipso*, PPh$_3$), 136.2 (C-4), 140.8 (C-7), 180.4 (C-3), 190.4 (C-1). ^{31}P NMR (CDCl$_3$): δ −2.06 (broad signal). Anal. Calcd for C$_{46}$H$_{38}$CuClOP$_2$S$_2$: C, 66.42; H, 4.60. Found: C, 69.03; H, 4.53.

General Procedure for the Synthesis of Bis{μ_2-[methyl-3-(*p*-methylphenyl)-3-hydroxy-2-propenedithioate-O,S]}bis(triphenylphosphine-P)dicopper(I) (7b). An ethanol suspension of bis(triphenylphosphine-P)[methyl-3-hydroxy-3-(*p*-methyl-phenyl)-2-propenedithioate-O,S]copper(I) (**6b**) (0.10 g, 0.12 mmol) was refluxed for 1 h. The dark red solid was filtrated and washed with ethyl acetate to obtain a crystalline product. Yield: 0.06 g (90%). Mp: 183−184 °C. IR (KBr, cm^{-1}): 3050 w, 1605 w, 1577 m, 1538 s, 1454 s, 1400 m, 1319 m, 1244 m, 1180 m, 1094 m, 935 m, 796 m, 774 m, 743 m, 694 s, 520 m, 499 m. FAB-MS+ (*m*/*z* %): 1159 ([M + Cu]$^+$, 13). ^{1}H NMR (CDCl$_3$): δ 2.39 (s, 3H, Me), 2.62 (s, 3H, H-8), 7.23 (d, 2H, J = 8.26 Hz, H-6), 7.24 (s, 1H, H-2), 7.42 (m, 9H, PPh$_3$), 7.58 (m, 6H, PPh$_3$), 7.85 (d, 2H, J = 8.26 Hz, H-5). ^{13}C NMR (CDCl$_3$): δ 16.8 (C-8), 21.6 (Me), 110.8 (C-2), 127.7 (C-6), 128.9 (d, $^3J_{PC}$ = 9.2 Hz, C-*m*, PPh$_3$), 129.1 (C-5), 130.3 (C-*p*, PPh$_3$), 132.4 (d, $^1J_{PC}$ = 36.7 Hz, C-*i*, PPh$_3$), 134.0 (d, $^2J_{PC}$ = 13.8 Hz, C-*o*, PPh$_3$), 139.1 (C-4), 141.4 (C-7), 182.2 (C-3), 190.0 (C-1). ^{31}P NMR (CDCl$_3$): δ 5.19 (broad signal).

Synthesis of Bis{μ_2-[methyl-3-phenyl-3-hydroxy-2-propenedithioate-O,S]}bis(triphenylphosphine-P)dicopper(I) (7c) Yield: 0.04 g (55%). Mp: 182−183 °C. IR (KBr, cm^{-1}): 3051 w, 1584 w, 1535 s, 1458 s, 1429 s, 1319 s, 1237 m, 1094 m, 934 m, 796 m, 774 m, 694 m, 622 m, 513 m. FAB-MS+ (*m*/*z* %): 1131 ([M + Cu]$^+$, 10). ^{1}H NMR (CDCl$_3$) δ 2.61 (s, 3H, H-8), 7.24 (s, 1H, H-2), 7.42 (m, 11H, H-7 + H-6 + PPh$_3$), 7.58 (m, 7H, PPh$_3$), 7.92 (m, 2H, H-5). ^{13}C NMR (CDCl$_3$) δ 16.9 (C-8), 110.9 (C-2), 127.6 (C-6), 128.4 (C-5), 128.9 (d, $^3J_{PC}$ = 10.4 Hz, C-*m*, PPh$_3$), 130.3 (C-*p*, PPh$_3$), 132.4 (d, $^1J_{PC}$ = 38.1 Hz, C-*i*, PPh$_3$), 134.0 (d, $^2J_{PC}$ = 16.2 Hz, C-*o*, PPh$_3$), 130.9 (C-7), 141.9 (C-4), 182.2 (C-3), 190.4 (C-1). ^{31}P NMR (CDCl$_3$): δ 5.13 (broad signal).

Synthesis of Bis{μ_2-[methyl-3-(*p*-fluorophenyl)-3-hydroxy-2-propenedithioate-O,S]}bis(triphenylphosphine-P)dicopper(I) (7d) Yield: 0.05 g (72%). Mp: 186−187 °C. IR (KBr, cm^{-1}): 3050 w, 1596 s, 1540 s, 1451 s, 1397 m, 1314 m, 1230 s, 1154 m, 1095 m, 936 m, 851 m, 780 s, 694 s, 495 m. FAB-MS+ (*m*/*z* %): 1167 ([M + Cu]$^+$, 7). ^{1}H NMR (CDCl$_3$): δ 2.62 (s, 3H, H-8), 7.08 (m, 2H, H-6), 7.19 (s, 1H, H-2), 7.42 (m, 9H, PPh$_3$), 7.75 (m, 6H, PPh$_3$),

Table 1. X-ray Crystallographic Data for Compounds **5b**, **6b**, **6e**, and **7b**

	5b	**6b**	**6e**	**7b**
formula	$C_{11}H_{12}OS_2$	$C_{47}H_{41}CuOP_2S_2$	$C_{46}H_{38}ClCuOP_2S_2$	$C_{58}H_{52}Cu_2O_2P_2S_4$
fw	224.33	811.40	831.81	1098.26
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	2	4	4	2
a (Å)	5.1192(5)	10.506(2)	10.4843(4)	12.678(3)
b (Å)	8.0297(8)	12.334(2)	12.306(1)	18.570(5)
c (Å)	14.459(1)	31.934(5)	31.777(1)	11.059(4)
α (deg)	82.664(2)	90.00	90.00	90.00
β (deg)	87.786(2)	93.63(1)	93.063(1)	98.54(2)
γ (deg)	74.965(2)	90.00	90.00	90.00
V (Å^3)	569.29(9)	4129.4(12)	4094.1(3)	2575.0(13)
d_{calcd} (g/cm^3)	1.309	1.305	1.350	1.416
T (K)	293	293	293	293
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	0.432	0.742	0.814	1.093
GOF on F^2	1.017	1.013	1.030	0.983
R^a (%) [$I > 2\sigma(I)$]	5.22	7.16	7.23	8.18
$R_w{}^b$ (%)	13.67	11.35	11.74	15.85

7.93 (m, 2H, H-5). ^{13}C NMR (CDCl$_3$): δ 16.8 (C-8), 110.6 (C-2), 115.3 (d, $^2J_{FC} = 22.9$ Hz, C-6), 129.9 (d, $^3J_{PC} = 9.2$ Hz, C-*m*, PPh$_3$), 128.9 (d, $^3J_{FC} = 22.9$ Hz, C-5), 130.4 (C-*p*, PPh$_3$), 132.3 (d, $^1J_{PC} = 34.4$ Hz, C-*i*, PPh$_3$), 133.9 (d, $^2J_{PC} = 16.0$ Hz, C-*o*, PPh$_3$), 137.9 (C-4), 166.2 (C-7), 180.2 (C-3), 190.9 (C-1). ^{31}P NMR (CDCl$_3$): δ 5.38 (broad signal).

Synthesis of Bis{μ_2-[methyl-3-(*p*-chlorophenyl)-3-hydroxy-2-propenedithioate-O,S]}bis(triphenylphosphine-P)dicopper(I) (7e) Yield: 0.05 g (78%). Mp: 188−189 °C. IR (KBr, cm^{-1}): 3050 w, 1580 m, 1537 m, 1450 s, 1311 m, 1240 m, 1091 m, 936 m, 793 m, 738 m, 695 m, 522 m. FAB-MS+ (*m*/*z* %): 1201 ([M + Cu]$^+$, 5). ^{1}H NMR (CDCl$_3$): δ 2.62 (s, 3H, H-8), 7.18 (s, 1H, H-2), 7.36 (d, 2H, $J = 6.61$ Hz, H-6), 7.42 (m, 9H, PPh$_3$), 7.56 (m, 6H, PPh$_3$), 7.85 (m, 2H, $J = 6.61$ Hz, H-5). ^{13}C NMR (CDCl$_3$): δ 16.8 (C-8), 110.5 (C-2), 128.5 (C-6), 128.9 (d, $^3J_{PC} = 11.5$ Hz, C-*m*, PPh$_3$), 129.0 (C-5), 130.4 (C-*p*, PPh$_3$), 132.4 (d, $^1J_{PC} = 36.9$ Hz, C-*i*, PPh$_3$), 134.0 (d, $^2J_{PC} = 16.2$ Hz, C-*o*, PPh$_3$), 136.9 (C-7), 140.3 (C-4), 180.5 (C-3), 191.8 (C-1). ^{31}P NMR (CDCl$_3$): δ 5.23 (broad signal).

X-ray Crystallography Structure Determination. Yellow single crystal of compound **5b**, red single crystals of compounds **6b** and **6e**, and dark red single-crystal compound **7b** were mounted on a glass fiber at room temperature. The crystals were then placed on Siemens P4/PC (**6b** and **7b**) and Bruker Smart Apex (**5b** and **6e**) diffractometers equipped with Mo Kα radiation; decay was negligible in both cases. Details of the crystallographic data collected on compounds **5b**, **6b**, **6e**, and **7b** are provided in Table 1. Systematic absences and intensity statistics were used in space group determination. All structures were solved using direct methods. Anisotropic structure refinements were achieved using full-matrix least-squares techniques on all non-hydrogen atoms. All hydrogen atoms (except H-1 of compound **5b**) were placed in idealized positions on the basis of hybridization, with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solutions and refinements were performed using SHELXTL version 6.10.[10]

Results and Discussion

Ligands 5a−e: Methyl 3-Hydroxy-3-(*p*-R-phenyl)-2-propenedithioate. The synthesis of methyl 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioate (R = MeO, Me, H, F, Cl) **5a−e** from corresponding dithio acids was carried out by a modified literature method.[6a] Dithioester ligands were identified by IR, MS−IE+ and ^{1}H NMR and they are in accordance with literature. The low yield of compound **5a** is due to a double methyl substitution of the dithio acid, which gives as a main product the corresponding ketene dithioacetal.[6,11]

Table 2. Selected Bond Distances (Å) and Bond Angles (°) of Compound **5b**

bond	distance	bond	angle
O1−C3	1.326(3)	C1−C2−C3	127.1(3)
C2−C3	1.358(4)	S1−C1−C2	126.2(2)
C1−C2	1.413(4)	S1−C1−S2	122.20(17)
C1−S1	1.664(3)	O1−C3−C2	123.0(3)
C1−S2	1.742(3)		

The ^{13}C NMR data for these compounds have not been described before. The spectra of compounds **5a−e** display a signal at δ 17.1, which was assigned to the S*Me* group. The vinyl carbon atom signal (C2) was observed at δ 107. All aromatic carbon signals appear in the region of δ 125−145. The signal at δ 169.0 ca. was assigned to the C-3 carbon atom; this signal is shifted downfield ($\Delta\delta \approx 3.0$) from the dithio acids because of a major electron density over this center. A signal around δ 217.0 was assigned to the C-1 dithioester carbon atom.[12] This signal is shifted upfield ($\Delta\delta \approx 7.0$) from the dithio acid compounds, which means a slight decrease in electron density over this center, which correlates well with the weak C=S vibration in IR and the incremental change in electron density of H-9 in ^{1}H NMR.

Crystal Structure of Compound 5b. The structure of ligand **5b** was fully established by X-ray diffraction analysis of a monocrystal obtained from a slow evaporation from hexane solution. The ORTEP view of compound **5b** is shown in Figure 1. Selected bond distances and bond angles are summarized in Table 2.

Compound **5b** is in enol form, showing an intramolecular hydrogen bond of O−H···S type. The O−H, S···H, and O···S bond distances and the O−H···S bond angle (Table 3), among the ^{1}H NMR chemical shift of H-9, allow us to

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(10) *SHELXTL*, version 6.10; Bruker Analytical X-ray Systems: Madison, WI, 2000.

(11) Ortega-Alfaro, M. C.; López-Cortés, J. G.; Toscano, R. A.; Alvarez-Toledano, C. *J. Braz. Chem. Soc.* **2005**, *16*, 362−371.

(12) Kanodia, S.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 469.

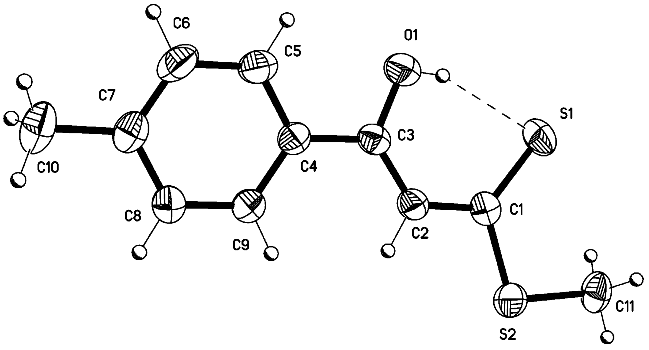

Figure 1. X-ray crystal structure of ligand **5b**. Ellipsoids are shown at the 30% probability level.

Table 3. Hydrogen Bonds for Compound **5b** (Å and deg)

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O(1)−H(1)···S(1)	0.78(3)	2.20(3)	2.938(3)	157(3)

Table 4. Hammett Linear Correlationship for Ligand **5** and Complexes **6** and **7**

	atom	equation	*r*	*s*	equation no.
Ligand **5**	C−1	$\delta = 217.1 + 3.97\,\sigma$	0.94	0.89	1
	C−3	$\delta = 168.9 - 3.86\,\sigma$	0.92	0.88	2
Complex **6**	C−1	$\delta = 190.1 + 6.21\,\sigma$	1.00	1.32	3
	C−1	$\Delta\delta^{a} = 27.1 - 2.24\,\sigma$	0.91	0.52	4
Complex **7**	C−1	$\delta = 190.6 + 4.86\,\sigma$	0.99	0.95	7
	C−3	$\delta = 181.8 - 4.76\,\sigma$	0.93	0.98	6

[a] $\Delta\delta = \delta_{\mathrm{complex}} - \delta_{\mathrm{ligand}}$ has been considered.

consider it as a strong hydrogen bond[13] similar to that of the monothio-β-diketones, in agreement with the RAHB theory.[14]

Electronic Correlation Analysis of Ligands 5a−e. To study the coordination capabilities of ligands **5a**−**e**, we applied correlation analysis with Hammett substituent constants (σ)[15] on the ^{13}C chemical shift of the C-1 and C-3 centers, which are linked to donor atoms. The found correlations are presented in Table 4.

The electron-withdrawing substituents in dithioester compounds increase the electron density over C-1 (eq. no. 1) and decrease it over C-3 (eq 2), as in dithio acid ligands.[5] This supports the π-delocalization on the fragment C1−C2−C3 and a coordinative behavior similar to that of the monothio-β-diketones.[16]

Copper(I) Complexes 6a−e. The syntheses of the copper(I) complexes (**6a**−**e**) from dithioester ligand **5** were carried out following the strategy showed in Scheme 1. The reaction of equivalent amounts of ligand **5** and bis(triphenylphosphine)copper(I) nitrate give an air-stable red crystalline solid. The complexes obtained (**6a**−**e**) were characterized by IR, MS−FAB+, and NMR techniques.

The IR spectra of copper complexes **6a**−**e** show the ν(C=C) vibration at 1520−1540 cm^{-1}, which is shifted to a wavenumber lower than that of free ligands **5** because of a major electron delocalization by complex formation. In the region of 1230−1320 cm^{-1}, the ν(C=S) vibration splits in two signals, maybe because of Fermi resonance.[17] The molecular ion [M^{+}] for complexes **5a**−**e** is not observed on the MS−FAB+ analysis; however, the adduct [M + Cu]$^{+}$ was detected, similar to that in copper(I) complexes **4**.[5]

The ^{1}H NMR spectra give a further insight in the coordination mode of the ligand and complex structure. The enol proton signal (H-9) disappears for the exchange of bis(triphenylphosphine)copper(I) cation. A single signal at δ 7.00 was assigned to vinyl proton H-2, slightly shifted upfield with respect to that of the ligand. Three multiple signals in the aromatic proton region were assigned to the coordinated triphenylphosphine molecules. These signals integrate for the 30 H that correspond to two coordinated triphenylphosphine molecules for each molecule of ligand.

The ^{13}C NMR data are a major support for the proposed coordination mode. In ^{13}C NMR spectra of copper(I) complexes **6**, a signal at $\delta \approx 190.0$ was assigned to C-1 and was shifted upfield ($\Delta\delta = 27.0$) with respect to that of the free ligands. The signal for the vinyl carbon atom C-2 at δ 110.0 stayed constant in all copper(I) complexes **6** and was slightly shifted downfield ($\Delta\delta = 2.7$) with respect to that of the free ligands. The signal assigned to the C-3 carbon atom at δ 181.0 was shifted downfield ($\Delta\delta = 12.4$) with respect to that of the free ligand. The triphenylphosphine carbon atoms were assigned according to (C−P) coupling constants *J*(C−P) for ortho and meta positions with $J = 16$ and 9 Hz, respectively.

The ^{31}P NMR spectra of complexes **6a**−**e** show a broad signal centered at δ −2. This signal was shifted upfield relative to that of the free triphenylphosphine (δ 4.0) because of the coordination of the phosphine to copper (I) center.

Crystal Structures of Compounds 6b and 6e. The structures of complexes **6** were fully established by the X-ray diffraction analyses of the **6b** and **6e** compounds. Red crystals of compounds **6b** and **6e** were obtained by slow diffusion in a MeOH−CH$_2$Cl$_2$ mixture. The ORTEP views of these complexes appear in Figures 2 and 3, respectively. Selected bond lengths and bond angles are summarized in Table 5.

The X-ray diffraction analysis for **6b** (Figure 2) shows the ligand coordinated to a copper center through O, S atoms in a six-member chelated ring. The copper atom forms a CuSOP$_2$ core with approximately tetrahedral symmetry. The ligand bite angle (96°) and the P1−Cu−P2 angle (113°) are the origin of distortion from tetrahedral symmetry. The angle

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(13) (a) Toullec, J. In *The Chemistry of the Enol*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1990; pp 323−398. (b) Steiner, T. *Chem. Commun.* **1998**, 411. (c) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565.

(14) (a) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023. (b) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917. (c) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909. (d) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405.

(15) March, J.; Smith, M. B. *March's Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; p 370.

(16) (a) Sreelata, C.; Gupta, V. D.; Narula, K. K.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 2623. (b) Siiman, O.; Titus, D. D.; Cowman, C. D.; Fresco, J.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 8097. (c) Silver, M. E.; Kyung Chun, H.; Fay, R. C. *Inorg. Chem.* **1982**, *21*, 3765.

(17) Yates, P.; Lynch, R.; Moore, R. D. *Can. J. Chem.* **1971**, *49*, 1467.

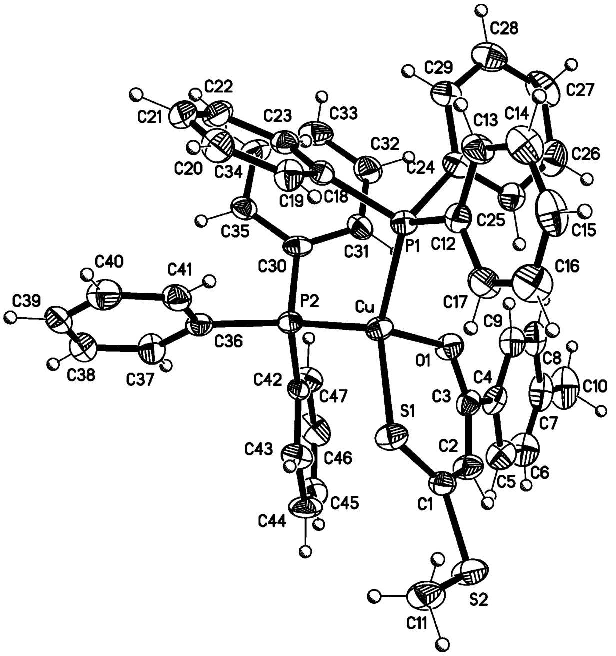


Figure 2. X-ray crystal structure of complex **6b**. Ellipsoids are shown at the 30% probability level.

P1−Cu−P2 is shorter than the reported values[18] for other bis(triphenylphosphine)copper(I) complexes. The π-delocalization of the chelated ring is evident in the analysis of related bond lengths (Table 5). The P−Cu bond distances are different, with P2−Cu (2.32 Å)[19] being longer than P1−Cu (2.24 Å).[20] Furthermore, P−Cu−S/O angles are different. However, in ^{31}P NMR spectra, only a broad signal was observed.[21] The structure of **6e** is identical to that of **6b.**

Electronic Correlation Analysis of Complexes 6a−e. The absolute value of the slope ρ of eq 3 for the C-1 carbon atom (Table 4) is greater than slope ρ of ligand eq 1 and has the same sign; this is probably because of an optimal overlap of copper and ligand orbitals, which enhances π-delocalization over the chelated ring with a major electronic influence over C-1.

Synthesis of Dinuclear Copper(I) Complexes 7. In the purification of complex **6b** by silica gel chromatography and in addition to **6b**, we obtained a new dark red compound (**7b**) in trace amounts that was not detected in the ^{1}H NMR spectrum of the crude reaction mixture of compound **6b**.

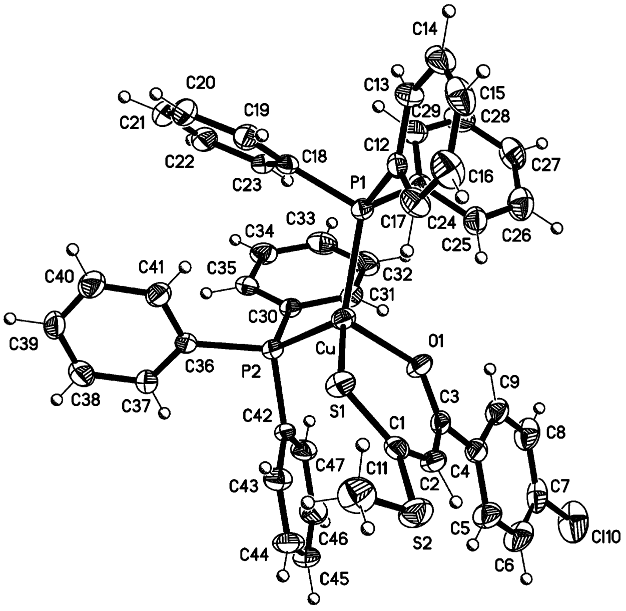


Figure 3. X-ray crystal structure of complex **6e**. Ellipsoids are shown at the 30% probability level.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for the Complexes **6b** and **6e**

Bond Distance (Å)

	6b	6e		6b	6e
Cu−O1	2.074(5)	2.071(3)	C3−C2	1.434(1)	1.410(6)
Cu−S1	2.280(2)	2.272(1)	C2−C1	1.362(1)	1.383(6)
P1−Cu	2.246(2)	2.245(1)	C1−S1	1.691(8)	1.680(5)
P2−Cu	2.326(2)	2.315(1)	C1−S2	1.790(8)	1.774(5)
O1−C3	1.264(8)	1.258(5)			

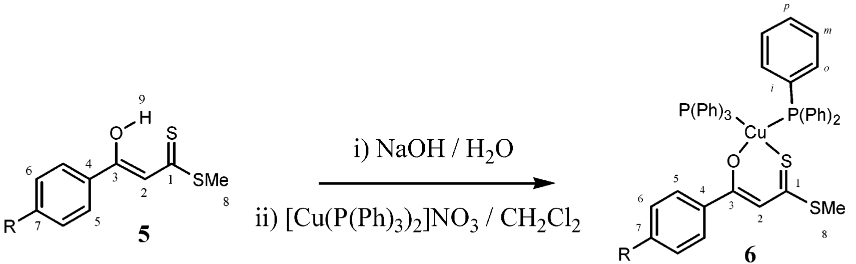
Bond Angles (deg)

	6b	6e		6b	6e
P1−Cu−P2	113.20(8)	113.45(5)	O1−Cu−P2	92.69(16)	92.2(1)
O1−Cu−S1	96.67(15)	97.3(1)	O1−Cu−P1	109.32(15)	110.0(1)
P1−Cu−S1	123.23(8)	122.50(5)	C1−C2−C3	129.0(7)	129.9(5)
P2−Cu−S1	114.96(8)	114.97(5)	S1−C1−S2	118.0(5)	119.0(3)

With the aim of improving the yield of **7b**, we tested some different reaction conditions and found that **7b** is obtained in good yield from **6b** in refluxing ethanol.

The reaction of complexes **6b−e** in refluxing ethanol produces compounds **7b−e** as crystalline dark red solids in good yields (Scheme 2). The complex **6a** is quite stable in

Scheme 1. Synthesis of Copper(I) Coordination Compounds **6a−e**



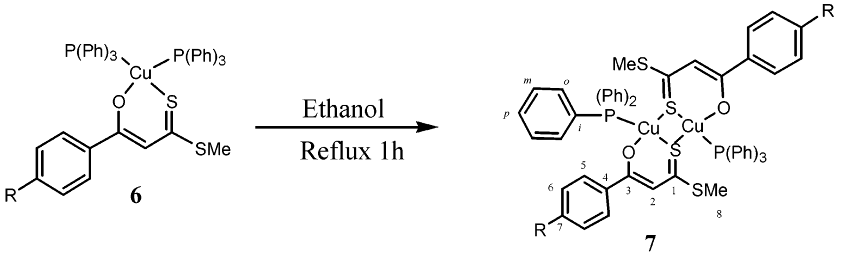
5

5a: R = MeO
5b: R = Me
5c: R = H
5d: R = F
5e: R = Cl

6

6a: R = MeO
6b: R = Me
6c: R = H
6d: R = F
6e: R = Cl

Scheme 2. Synthesis of Copper(I) Dinuclear Complexes **7b**−**e**



7b: R = Me
7c: R = H
7d: R = F
7e: R = Cl

such conditions despite 25 h of refluxing. Compounds **7b**−**e** were characterized by IR, MS−FAB+, and NMR techniques.

In general, the IR spectra of complexes **7b**−**e** show a decrease in the relative intensity of phosphine signals. Similar to the spectra for complexes **6a**−**e,** two bands at 1320−1230 cm^{-1} were assigned to the ν(C═S) vibration;[22] these bands were shifted to lower wavenumbers than in **6a**−**e**. The band at 1235 cm^{-1} is the most affected with respect to complexes **6b**−**e** ($\Delta\nu \approx 50$ cm^{-1}) because of a major electron contribution to metal center.

The ^{1}H NMR spectra of compounds **7b**−**e** show a 1:1 relation of ligand:triphenylphosphine signals, corresponding to a copper(I) tricoordinated species. However, taking into account that four-coordinated copper(I) complexes are more stable than tricoordinated species[23] and the $[Cu_3L_2(PPh_3)_2]^+$ fragment in the FAB analyses, we proposed a dimeric species for complexes **7**. Additionally, in ^{1}H NMR spectra of compounds **7b**−**e,** a single signal assigned to the MeS group (H-8) is observed at δ 2.6. The signal around δ 6.9 (H-2) is shifted downfield with respect to that of complex **6** ($\Delta\delta \approx$ 0.3). The multiple signals at δ 7.62 and 7.42 were identified as being aromatic proton signals of triphenylphosphine molecules. These signals are shifted downfield with respect to those of complexes **6** because only one phosphine molecule is coordinated to the copper(I) center. The integral of these signals corresponds to 15 H, supporting the presence of one molecule of triphenylphosphine.

The ^{13}C NMR spectra of complexes **7b**−**e** are quite similar to those of complexes **6b**−**e**. The main differences are in the coupling constants *J*(C−P) of the triphenylphosphine carbon atoms. The signal at δ 129 ($^3J_{CP} = 10$ Hz) was assigned to C-*meta*. A single signal at δ 130 was assigned to C-*para*, and a signal at δ 132 ($^1J_{CP}$ 34−38 Hz ca.) was assigned to C-*ipso*. The C-*ortho* appeared at δ 134 ($^2J_{CP} =$ 16 Hz). The value of the $^1J_{CP}$ coupling constant notably increases with respect to that of complex **6**, probably because of a major s-character on the phosphorus atom by the coordination; this points to an increase in the P−Cu covalent bond character.[24]

The ^{31}P NMR spectra at room temperature show a broad signal centered at δ 5.2 with two equivalent phosphorus atoms. This signal is clearly shifted downfield ($\Delta\delta = 7.2$) with respect to that of complexes **6b**−**e** (δ −2.0 ca.).

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) of Compound **7b**

Bond Distances (Å)			
Cu1−O1	2.057(7)	C1−S1	1.716(10)
Cu1−P1	2.227(3)	C1−S2	1.742(9)
Cu1−S1	2.307(3)	O1−C3	1.240(12)
Cu1−S1A	2.441(3)	C1−C2	1.401(14)
Cu1−Cu1A	2.648(3)	C2−C3	1.392(15)
Bond Angles (deg)			
O1−Cu1−S1	96.8(2)	P1−Cu1−O1	115.7(2)
Cu1−S1−Cu1A	67.71(9)	P1−Cu1−S1	118.30(12)
S1−Cu1−S1A	112.29(9)	P1−Cu−S1A	116.87(10)
O1−Cu1−S1A	92.2(2)	C1−C2−C3	133.1(10)

Crystal Structure of Compound 7b. The dinuclear structure of complex **7** was fully established by X-ray diffraction analysis of complex **7b**. A dark red crystal of compound **7b** was obtained by slow diffusion on a MeOH−CH_2Cl_2 system. Selected bond distances and bond angles are summarized in Table 6, and the ORTEP view of complex **7b** is shown in Figure 4.

The X-ray diffraction analysis of complex **7b** shows a copper(I) dinuclear compound with two sulfur atoms forming a bridge between both copper atoms in a Cu_2S_2 square planar arrangement that contains the inversion center of the molecule. To the best of our knowledge, the stability of the Cu_2S_2 moiety depends of the S−S and Cu−Cu intermolecular interactions[25] among the ligands bonded to the copper center.[26] In general, the S−S is more important than the Cu−Cu interaction. However, in compound **7b**, the Cu−Cu distance (2.648(3) Å) is smaller than the sum of the van der Waals radius (2.80 Å), which makes it more significant than the S−S interaction in the Cu_2S_2 moiety.

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(18) (a) Jian, F.; Bei, F.; Lu, L.; Yang, X.; Wang, X.; Razak, I. A.; Sundara Raj, S.; Fun, H.-K. *Acta Crystallogr., Sect. C* **2000**, *56*, e288. (b) Deivaraj, T. C.; Vittal, J. J. *Acta Crystallogr., Sect. E* **2001**, *57*, m566.

(19) Lippard, S. J.; Palenik, G. J. *Inorg. Chem.* **1971**, *10*, 1322.

(20) Yang, R.-N.; Wang, D.-M.; Lui, Y.-F.; Jin, D.-M. *Polyhedron* **2001**, *20*, 585.

(21) (a) Lobana, T. S.; Paul, S.; Castineiras, A. *Polyhedron* **1997**, *16*, 4023. (b) Deivaraj, T. C.; Lai, G. X.; Vittal, J. J. *Inorg. Chem.* **2000**, *39*, 1028. (c) Marchetti, F.; Pettinari, C.; Pettinari, R.; Cingolani, A.; Camalli, M.; Spagna, R. *Inorg. Chim. Acta* **2000**, *299*, 65.

(22) Duguay, G.; Quiniou, H. *Bull. Soc. Chim. Fr.* **1972**, 637.

(23) Livingstone, S. E. In *Comprehensive Coordination Chemistry*; Willkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; p 584.

(24) Iggo, J. A. *NMR Spectroscopy in Inorganic Chemistry;* Oxford University Press: New York, 1999; p 41−48.

(25) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187.

(26) (a) Karagiannidis, P.; Hadjikakou, P.; Aslanidis, P.; Hountas, A. *Inorg. Chim. Acta* **1990**, *178*, 27. (b) Lobana, T. S.; Paul, S.; Castineiras, A. *Polyhedron* **1997**, *16*, 4023.

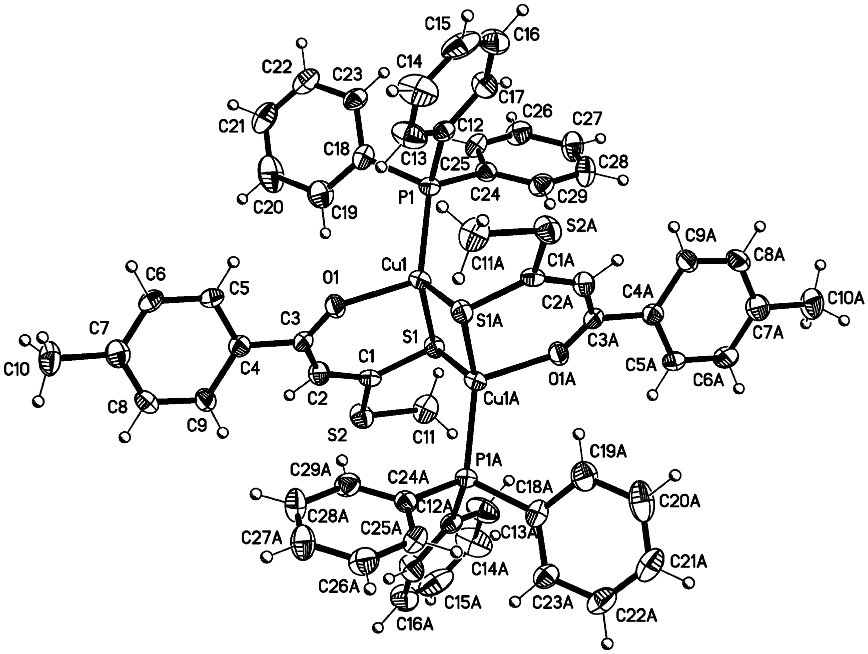

Figure 4. X-ray crystal structure of dinuclear complex **7b**. Ellipsoids are shown at the 30% probability level.

Each copper atom is bonded to the ligand in a six-membered chelated ring and to a triphenylphosphine molecule, forming a CuS_2OP core with tetrahedral symmetry distorted only by the bite angle of the ligand (96.8°). Most of the bond distances around the copper atom are similar to those of complexes **6b** and **6e**.

Generally, chalcogen-bridged copper(I) clusters have been obtained from the reaction of equivalent amounts of copper(I) and ligand.[27] The synthesis of dinuclear copper(I) complexes from mononuclear copper(I) compounds may be a novel strategy in copper(I) cluster chemistry.

Conclusions

In summary, five new copper(I) compounds (**6a**−**e**) were obtained from the reaction of ligands **5a**−**e** and bis(triphenylphosphine)copper(I) nitrate; the expected O,S-coordination was confirmed by the X-ray diffraction analysis of **6b** and **6e**. The Hammett correlation analyses of complexes **6a**−**e** display the major electronic influence of the substituent on the C-1 carbon atom, probably because of the optimal overlap of copper−ligand orbitals.

In addition, the ethanol refluxing of complexes **6b**−**e** yields four novel copper(I) dinuclear compounds **7b**−**e**, which could be a novel strategy in copper(I) cluster chemistry. The structure of complex **7** was proposed on the basis of FAB and NMR analyses and totally confirmed by X-ray diffraction analysis of compound **7b**.

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Supporting Information Available: Complete details of the X-ray diffraction study of compounds **5b**, **6b**, **6e**, and **7b** (CIF) and NMR chemical shifts of complex **6a**−**e** and **7b**−**e** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) (a) Ho, R. K. Y.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1966**, *19*, 1179. (b) Chaston, S. H. H. *Aust. J. Chem.* **1967**, *20*, 1065. (c) Livingstone, S. E. *Coord. Chem. Rev.* **1971**, *7*, 59. (d) Dance, I. G.; Scudder, M. L.; Fitzpatrick, L. J. *Inorg. Chem.* **1985**, *24*, 2547. (e) Constable, E. C.; Elder, S. M.; Palmer, C. A.; Raithby, P. R.; Tocher, D. A. *Inorg. Chim. Acta* **1996**, *252*, 281. (f) Shakir, M.; Kumar, D.; Varkey, S. P. *Polyhedron* **1992**, *11*, 2831. (g) Develaux-Nicot, B.; Mathieu, R.; de Montauzon, D.; Lavigne, G.; Majoral, J.-P. *Inorg. Chem.* **1994**, *33*, 434. (h) Develaux-Nicot, B.; Lugan, N.; Mathieu, R.; Majoral, J.-P. *Inorg. Chem.* **1992**, *31*, 334.