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Article

Synthesis, Characterization, and Tautomerism of Four Novel Copper(I) Complexes from 3-Hydroxy-3-(*p*-R-phenyl)-2-propenedithioic Acids

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The paper describes the synthesis and structural characterization of four novel copper(I) complexes $[CuL(PPh_3)_2]$ (L = 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioate). In addition, a tautomeric equilibrium in solution was found and Hammett correlations with ^{13}C NMR parameters were studied. The structure of one complex was fully established by X-ray diffraction analysis.

Introduction

The reaction between methyl ketones and CS_2 produces the corresponding dithio acid compounds, which can present a keto−enol equilibrium in solution[1] (Scheme 1). This equilibrium is generally favored toward the chelating enol form, when R = phenyl, because of its energetical stability.[2]

The 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioic acid has shown different applications such as being the active moiety in ionic resins for transition metal ion separations,[3,4] in the development of new Ag$^+$-selective membrane electrodes,[5,6] and as hair-growing agents using Zn as metallic center,[7] among others. But in all cases, the complex structures have not been determined.

Scheme 1. Reaction of Methyl Ketones with CS_2

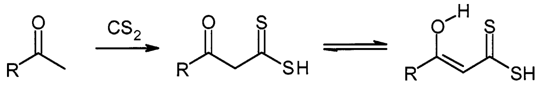
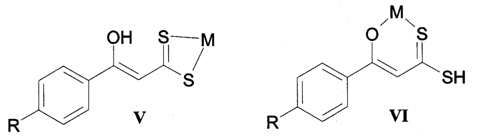


Chart 1. Possible Coordination Modes for 3-Hydroxy-3-(*p*-R-phenyl-2-propenedithioic Acids



Weigand,[8] Coucouvanis,[9,10] and Lih[3] have proposed two possible coordination modes (**V** and **VI**) for these kinds of ligands (Chart 1); however, only a few examples displaying S,S-coordination have been reported for Ni(II), Pd(II), Pt(II),[8,11,12] and Fe(0)[13,14] complexes (Chart 2).

As a part of our studies with **1a**−**d** and with the aim of understanding the factors that govern the reactivity of these ligands toward transition metals, we herein report the

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(1) Dunn, A. D.; Rudorf, W.-D. *Carbon disulphide in Organic Chemistry*; Ellis Harwood: Chichester, U.K., 1989; p 120.

(2) Saquet, M.; Thuillier, A. *Bull. Soc. Chim. Fr*. **1967**, 2841.

(3) Liu, C.-Y.; Lih, J.-J. *Fresenius' J. Anal. Chem.* **1988**, *332*, 171.

(4) Lih, J. J.; Yeh, K. Y.; Liu, C. Y. *Fresenius' J. Anal. Chem.* **1990**, *336*, 12.

(5) Galan-Vidal, C. A.; Paez-Hernandez, M. E.; Cuellar-Cruz, M.; Perez-Lopez, B.; Lopez-Martinez, E.; Pliego-Canton, T. C.; Alvarez Toledano, C. *Sens. Chemom.* **2001**, 39.

(6) Galan-Vidal, C. A.; Paez-Hernandez, M. E.; Cuellar-Cruz, M.; Perez-Lopez, B.; Portillo-Ortega, G.; Alvarez-Toledano, C. *Rev. Mex. Fis.* **2000**, *46* (Supl. 2), 132.

(7) Oda, Y.; Kubota, S.; Hiraga, K.; Koga, H.; Niwano, Y. *Jpn. Kokai Tokkyo Koho* **1995**, 14; *Chem. Abstr.* **1996**, *124*, 74794.

(8) Weignad, W.; Bosl, K.; Polborn, K. *Chem. Ber.* **1990**, *123*, 1339.

(9) Coucouvanis, D.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 1346.

(10) Caffery, M. L.; Coucouvanis, D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2081.

(11) Weigand, W.; Saumweber, R.; Schulz, P. *Z. Naturforsch*. **1993**, *48b*, 1080.

(12) Buchweitz, J.; Gompper, R.; Polborn, K.; Robl, C.; Sailer, M.-T.; Weigand, W. *Chem. Ber.* **1994**, *127*, 23.

(13) 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.

(14) Alvarez-Toledano, C.; Delgado, E.; Donnadieu, B.; Hernández, E.; Martín, G.; Zamora, F. *Inorg. Chim. Acta* **2003**, *351*, 119.

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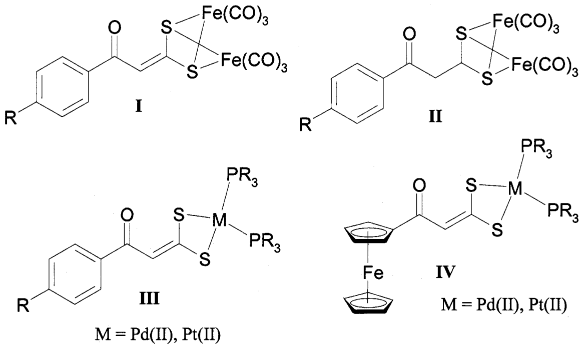
Chart 2. Reported Complexes for 3-Hydroxy-2-propenedithioate Ligands



synthesis of novel copper(I) complexes of type [CuL(PPh$_3$)] (L = 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioate).

Experimental Section

Materials. FTIR spectra were recorded on either a Perkin-Elmer 283 B or a Perkin-Elmer 1420 spectrophotometer in KBr. Melting points were measured on a Melt-Temp II apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a JEOL Eclipse +300 using CDCl$_3$ as solvent. Chemical shifts were reported in δ relative to TMS for ^{1}H and ^{13}C and 30% H$_3$PO$_4$ for ^{31}P. The MS-FAB$^+$ spectra were obtained on a JEOL JMS SX 102A. The 3-hydroxy-3-(*p*-R-phenyl)-2-propenedithioic acid **1a**−**d** were synthesized by Larsson's method.[15] Bis(triphenylphosphine)copper(I) nitrate was obtained as reported in the literature.[16] The keto−enol tautomerism was studied by ^{1}H, ^{13}C, COSY, and HETCOR NMR experiments.

Synthesis of 3-Hydroxy-3-(*p*-methylphenyl)-2-propenedithioic Acid (1a). Yield: 5.3 g (75%). Mp: 85−86 °C (lit. mp: 85 °C). IR (KBr, cm^{-1}): 3433.0 w, 2920.1 w, 2544.0 w, 2497.7 w, 1605.1 m, 1581.7 m, 1551.1 s, 1502.7 m, 1426.7 m, 1251.1 s, 956.5 m, 836.5 m, 785.5 s, 674.6 m. ^{1}H NMR (CDCl$_3$): δ 2.41 (s, 3H, Me), 5.38 (s, 1H, H-9), 6.95 (s, 1H, H-2), 7.26 and 7.77 (AA′BB′ system, 4H, J = 8.26 Hz, H-6, H-5), 15.38 (s, 1H, H-8). ^{13}C NMR (CDCl$_3$): δ 21.8 (Me), 107.9 (C-2), 127.1 (C-5), 129.8 (C-6), 130.8 (C-4), 143.8 (C-7), 173.3 (C-3), 210.4 (C-1).

3-Hydroxy-3-phenyl-2-propenedithioic Acid (1b). Yield: 1.8 g (62%). Mp: 86−89 °C (lit. mp: 63 °C). IR (KBr, cm^{-1}): 3430.8 w, 2512.1 w, 1591.1 m, 1550.2 s, 1486.6 m, 1452.8 m, 1244.5 s, 912.4 m, 822.9 m, 757.9 s, 678.9 m. ^{1}H NMR (CDCl$_3$): δ 5.42 (s, 1H, H-9), 6.96 (s, 1H, H-2), 7.46 (m, 2H, H-6), 7.55 (m, 1H, H-7), 7.87 (m, 2H, H-5), 15.36 (s, 1H, H-8). ^{13}C NMR (CDCl$_3$): δ 108.2 (C-2), 127.0 (C-6), 129.0 (C-5), 132.7 (C-7), 133.8 (C-4), 172.9 (C-3), 211.4 (C-1).

3-Hydroxy-3-(*p*-fluorophenyl)-2-propenedithioic Acid (1c). Yield: 2.0 g (12%). Mp: 67−70 °C (lit. mp: 74 °C). IR (KBr, cm^{-1}): 2495.5 w, 1593.9 s, 1562.3 s, 1434.2 m, 1228.0 s, 1157.2 m, 960.3 m, 841.3 m, 773.5 m, 572.5 m. ^{1}H NMR (CDCl$_3$, 298 K): δ 5.42 (s, 1H, H-9), 6.89 (s, 1H, H-2), 7.14 (m, 2H, H-6), 7.88 (m, 2H, H-5), 15.35 (s, 1H, H-8). ^{13}C NMR (CDCl$_3$): δ 107.9 (s, C-2), 116.3 (d, $^2J_{C-F}$ = 21.92 Hz, C-6), 129.4 (d, $^3J_{C-F}$ = 9.23 Hz, C-5), 129.9 (C-4), 165.5 (d, $^1J_{C-F}$ = 261.34 Hz, C-7), 171.7 (C-3), 211.4 (C-1).

3-Hydroxy-3-(*p*-chlorophenyl)-2-propenedithioic Acid (1d). Yield: 2.5 g (14%). Mp: 88−91 °C (lit. mp: 99.5 °C). IR (KBr, cm^{-1}): 2549.8 w, 2518.2 w, 1682.8 w, 1591.8 s, 1557.3 s, 1485.1 s, 1421.4 s, 1240.3 s, 1096.3 s, 968.5 s, 935.3 s, 774.2 vs, 736.9 m, 645.4 m, 545.3 m. ^{1}H NMR (CDCl$_3$): δ 5.46 (s, 1H, H-9), 6.90 (s, 1H, H-2), 7.44 and 7.81 (AA′BB′ system, 4H, J = 8.72 Hz, H-6, H-5), 15.32 (s, 1H, H-8). ^{13}C NMR (CDCl$_3$): δ 107.9 (C-2), 128.3 (C-5), 129.3 (C-6), 132.2 (C-4), 138.9 (C-7), 171.4 (C-3), 211.8 (C-1).

General Procedure. Synthesis of (3-Hydroxy-3-(*p*-methylphenyl)-2-propenedithioate-*S*,*S*′)bis(triphenylphosphine-*P*)copper(I) (2a). A 1 equiv (0.56 mmol) amount of Cu(PPh$_3$)$_2$NO$_3$ in CH$_2$Cl$_2$ was added to an aqueous solution of ligand 1a (0.56 mmol) and NaOH (0.56 mmol). The original orange organic solution became dark-red. The mixture was stirred for 15 min, and then the organic layer was dried with Na$_2$SO$_4$. The solvent was distilled under vacuum. Then, ethanol was added to precipitate the complex, which was filtered out and dried under vacuum to obtain a red solid. Yield: 0.15 g (34%). Mp: 182−183 °C. IR (KBr, cm^{-1}): 3449.8 s, 3051.8 s, 1581.5 vs, 1556.3 vs, 1505.3 vs, 1433.5 vs, 1210.9 vs, 1093.9 s, 1038.7 vs, 981.2 s, 745.2 vs, 694.3 vs, 508.8 vs. FAB MS: m/z 859.0, [M + Cu]$^+$. HR FAB (m/z): calcd for $C_{46}H_{39}Cu_2OP_2S_2$, 859.0510; found, 859.0472. Anal. Calcd for $C_{46}H_{39}CuOP_2S_2$: C, 69.3; H, 4.9. Found: C, 67.1; H, 4.9. ^{1}H NMR (CDCl$_3$): δ 2.37 (s, 3H, Me, keto), 2.40 (s, 3H, Me, enol), 4.59 (s, 2H, H-2, keto), 6.88 (s, 1H, H-2, enol), 7.20 and 7.72 (AA′BB′ system, 4H, J = 8.07 Hz, H-6, H-5, enol), 7.22 and 8.06 (AA′BB′ system, 4H, J = 8.07 Hz, H-6, H-5, keto,), 7.25 (m, PPh$_3$), 13.01 (s, 1H, H-8, enol). ^{13}C NMR (CDCl$_3$): δ 21.6 (Me, keto), 21.7 (Me, enol), 66.1 (C-2, keto), 113.2 (C-2, enol), 126.3 (C-6, enol), 126.5 (C-5, enol), 128.5 (aromatic, PPh$_3$ + C-5, keto), 129.2 (C-6, keto), 129.5 (aromatic, PPh$_3$), 132.9 (C-4, enol,), 134.7 (C-4, keto,), 140.8 (C-7, enol,), 143.7 (C-7, keto,), 163.2 (C-3), 193.4 (C-1). ^{31}P NMR (CDCl$_3$) δ 0.01 (broad signal).

(3-Hydroxy-3-phenyl-2-propenedithioate-*S*,*S*′)bis(triphenylphosphine-*P*)copper(I) (2b). Yield: 0.12 g (27%). Mp: 166−167 °C. IR (KBr, cm^{-1}): 3432.2 w, 3052.1 w, 1681.1 w, 1585.9 m, 1558.9 s, 1484.1 m, 1432.2 m, 1206.3 m, 1093.6 m, 1044.3 m, 987.3 m, 745.5 m, 693.2 s, 497.2 m. FAB MS: m/z 845.0, [M + Cu]$^+$. HR FAB (m/z): calcd for $C_{45}H_{37}Cu_2OP_2S_2$, 845.0353; found, 845.0369. Anal. Calcd for $C_{45}H_{37}CuOP_2S_2$: C, 69.0; H, 4.8. Found: C, 68.7; H, 4.9. ^{1}H NMR (CDCl$_3$): δ 4.62 (s, 2H, H-2, keto), 6.89 (s, 1H, H-2, enol), 7.25 (m, PPh$_3$), 7.47 (t, H-6, enol), 7.42 (m, 2H, H-6, keto), 7.53 (m, 2H, H-7, keto + enol), 7.96 (m, 2H H-5, enol), 8.17 (m, 2H, H-5, keto), 13.04 (s, 1H, H-8, enol). ^{13}C NMR (CDCl$_3$): δ 66.1 (C-2, keto), 113.6 (C-2, enol), 126.4 (C-5, enol), 128.2 (C-6, enol), 128.5 (aromatic, PPh$_3$ + C-6, keto), 128.6 (aromatic, PPh$_3$), 129.5 (C-5, enol), 130.4 (C-7, enol), 132.9 (C-7, keto), 133.7 (aromatic, PPh$_3$), 135.8 (C-4, enol), 136.9 (C-4, keto), 162.9 (C-3), 193.7 (C-1). ^{31}P NMR (CDCl$_3$): δ 0.31 (broad signal).

(3-Hydroxy-3-(*p*-fluorophenyl)-2-propenedithioate-*S*,*S*′)bis(triphenylphosphine-*P*)copper(I) (2c). Yield: 0.32 g (60%). Mp: 176−178 °C. IR (KBr, cm^{-1}): 3440.7 w, 3045.7 w, 1678.5 w, 1594.9 s, 1565.2 s, 1499.7 s, 1432.2 s, 1227.0 s, 1201.5 s, 1154.4 s, 1092.7 s, 1034.2 s, 981.3 m, 843.3 s, 743.4 s, 693.3 s, 510.1 s. FAB MS: m/z 863.0, [M + Cu]$^+$. HR FAB (m/z): calcd for $C_{45}H_{36}Cu_2FOP_2S_2$, 863.0259; found, 863.0270. Anal. Calcd for $C_{45}H_{36}CuFOP_2S_2$: C, 67.4; H, 4.5. Found: C, 67.1; H, 4.7. ^{1}H NMR (CDCl$_3$): δ 4.57 (s, 2H, H-2, keto), 6.83 (s, 1H, H-2, enol), 7.06 (m, 4H, H-6, keto + enol), 7.25 (m, PPh$_3$), 7.79 (m, 2H, H-5, enol), 8.18 (m, 2H, H-5, keto), 13.04 (s, 1H, H-8, enol). ^{13}C NMR (CDCl$_3$): δ 66.2 (C-2, keto), 113.4 (C-2, enol), 115.6 (C-6, $^2J_{C-F}$ = 21.8 Hz, enol + keto), 128.5 (aromatic, PPh$_3$), 129.7 (aromatic, PPh$_3$), 131.9 (C-4, enol), 132.1 (C-5, $^3J_{C-F}$ = 9.2 Hz, keto + enol), 133.4 (C-4, keto), 133.7 (aromatic, PPh$_3$), 161.8 (C-3), 164.1 (C-

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(15) Larsson, F. C. V.; Lawesson, S.-O. *Tetrahedron* **1972**, *28*, 5341.

(16) (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.

Table 1. X-ray Crystallographic Data for Complex **2a**

formula	$C_{46}H_{39}CuOP_2S_2$
fw	797.37
cryst system	monoclinic
space group	$P2_1/c$
Z	4
a, Å	13.947(2)
b, Å	10.828(2)
c, Å	26.508(3)
β, deg	92.750(1)
V, Å^3	3998.6(1)
d_{calcd}, g/cm^3	1.325
temp, K	293
wavelength, Å	0.710 73
abs coeff, mm^{-1}	0.765
goodness of fit on F^2	1.014
R,[a] %	5.87
R_w,[b] %	10.28

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

7, $^1J_{C-F}$ = 251.5 Hz, enol), 165.7 (C-7, $^1J_{C-F}$ = 251.5 Hz, keto), 192.1 (C-1). ^{31}P NMR ($CDCl_3$): δ 0.50 (broad signal).

(3-Hydroxy-3-(*p*-chlorophenyl)-2-propenedithioate-*S*,*S′*)bis(triphenylphosphine-*P*)copper(I) (2d). Yield: 0.50 g (54%). Mp: 150−154 °C. IR (KBr, cm^{-1}): 3442.1 w, 3051.8 w, 1680.0 w, 1584.0 s, 1553.6 s, 1483.4 s, 1434.1 s, 1238.2 m, 1209.8 s, 1093.0 s, 1036.6 s, 985.0 m, 819.9 m, 744.7 s, 694.4 s, 510.1 s. FAB MS: *m*/*z* 879.0, [M + Cu]$^+$. HR FAB (*m*/*z*): calcd for $C_{45}H_{36}ClCu_2OP_2S_2$, 878.9963; found, 878.9956. Anal. Calcd for $C_{45}H_{36}ClCuOP_2S_2$: C, 66.1; H, 4.4. Found: C, 64.9; H, 4.5. ^{1}H NMR ($CDCl_3$): δ 4.55 (s, 2H, H-2, keto), 6.82 (s, 1H, H-2, enol), 7.25 (m, PPh_3), 7.35 and 8.08 (AA′BB′ system, 4H, J = 8.07 Hz, H-6, H-5, keto), 7.35 and 7.72 (AA′BB′ system, 4H, J = 7.67 Hz, H-6, H-5, enol), 13.02 (s, 1H, H-8, enol). ^{13}C NMR ($CDCl_3$): δ 66.2 (C-2, keto), 113.6 (C-2, enol), 127.6 (C-6, keto), 128.5 (aromatic, PPh_3), 128.8 (C-5, enol), 129.6 (aromatic, PPh_3), 130.8 (C-5, enol), 130.9 (C-6, keto), 133.8 (aromatic, PPh_3), 134.3 (C-7, enol), 135.3 (C-4, enol), 136.3 (C-4, keto), 139.3 (C-7, keto), 161.3 (C-3), 192.5 (C-1). ^{31}P NMR ($CDCl_3$): δ 0.03 (broad signal).

X-ray Crystallography. Red crystals of compound **2a** were obtained by slow diffusion of dichloromethane/methanol system at room temperature. Details of crystal data collected are provided in Table 1. The structure was 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) were placed in ideal positions on the basis of hybridization, with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solution and refinements were performed using SHELXTL V 6.10.[17] Selected bond distances and bond angles for compound **2a** are given in Tables 5 and 6.

Results and Discussion

The syntheses of copper(I) complexes were carried out by following Scheme 2. The reaction of 3-hydroxy-3-(*p*-methylphenyl)-2-propenedithioic acid (**1a**) with bis(triphenylphosphine)copper(I) nitrate, at room temperature, yields a stable red crystalline solid. The structure for complex **2a** was assigned according to spectroscopy data.

IR spectrum of **2a** shows the ν(C=S) vibration (1251 cm^{-1}) shifted substantially to lower wavenumber than those of the free ligand [ν(C=S) 1210 cm^{-1}, $\Delta\nu$ = 41 cm^{-1}]. This means that coordination of ligand **1a** to the cationic Lewis acid bis(triphenylphosphine)copper(I) leads to a decrease the C=S bond strength.[18] A similar behavior has been observed in analogous Ni(II), Pd(II), and Pt(II) complexes[8,9] and copper(I) thiourea complexes.[19] The characteristic triphenylphosphine vibrations were observed at 1433, 1094, 745, and 694 cm^{-1}.

Scheme 2. Preparation of Copper(I) Coordination Compounds **2a**−**d**

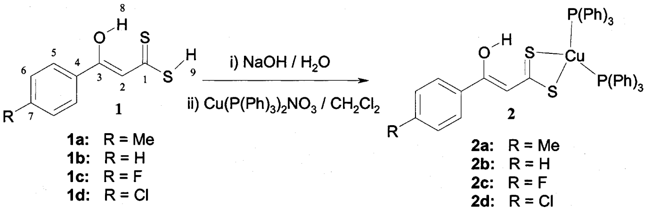

Table 2. ^{1}H and ^{13}C NMR Chemical Shifts for Ligands **1a**−**d**

atom	**1a**	**1b**	**1c**	**1d**
		δ(^{1}H)		
H-9	5.38	5.42	5.42	5.45
H-2	6.95	6.96	6.89	6.90
H-6	7.26	7.46	7.14	7.44
H-5	7.77	7.87	7.88	7.81
H-8	15.38	15.35	15.35	15.38
		δ(^{13}C)		
C-2	107.9	108.2	107.9	107.9
C-6	129.8	127.0	116.3	129.3
C-4	130.8	133.8	129.9	132.2
C-5	127.1	129.0	129.4	128.3
C-7	143.8	132.7	165.5	138.9
C-3	173.3	172.9	171.7	171.4
C-1	210.4	211.4	211.4	212.1

The molecular ion is not observed in the FAB$^+$ mass spectrum of **2a**; however, a peak that corresponds to the adduct of the expected molecular ion with a copper atom [M + Cu]$^+$ appeared at *m*/*z* 859. The isotopic distribution of this species is in agreement with the calculated composition. The second copper ion may be bonded through the already coordinated sulfur atoms of the complex by means of a weak interaction, as it was observed in other sulfur complexes.[14,20] Likewise, a peak at *m*/*z* 534, assigned to the fragment [M$^+$ − PPh_3], was observed.

The ^{1}H NMR spectrum of **2a** presents several differences in comparison to **1a** (Table 2). The enolic proton signal H-8 in **1a** is shifted upfield from δ 15.38 to 13.01, which is due to the coordination of sulfur to the copper and hence a decrease of electronic density on the sulfur atom. The corresponding signal for the vinylic proton is observed at δ 6.88.

The ^{13}C NMR data provided further evidence supporting this coordinating pattern. The signal attributed to C-1 and C-3 in the ligand **1a** are shifted upfield in the complex **2a** from δ 210.4 and 173.3 to 193.4 and 163.2, respectively, while the assigned signal to the vinylic carbon atom C-2 is shifted downfield from δ 107.9 to 113.2. These shifts are

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

(18) Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds. Part B*, 5th ed.; J. Wiley: New York, 1997; p 1.

(19) Bombicz, P.; Mutikainen, I.; Krunks, M.; Leskelä, T.; Madarász, J.; Miiniströ, L. *Inorg. Chim. Acta* **2004**, *357*, 513.

(20) Coucouvanis, D.; Piltingsrud, D. *J. Am. Chem. Soc.* **1973**, *95*, 5556. (b) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G. *Inorg. Chem.* **2001**, *40*, 2051. (c) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 6193.

Table 3. ^{1}H and ^{31}P NMR Chemical Shifts and K_{eq} at T_{amb} for Complexes **2a−d**

			2a	2b	2c	2d
δ(^{1}H)	keto (3)	H-2	4.59	4.62	4.57	4.55
		H-6	7.22	7.42	7.06	7.35
		H-5	8.06	8.17	8.18	8.08
		phosphines	7.15−7.45	7.15−7.35	7.10−7.40	7.10−7.40
	enol (2)	H-2	6.88	6.89	6.83	6.82
		H-6	7.20	7.47	7.06	7.35
		H-5	7.72	7.96	7.79	7.72
		H-8	13.01	13.04	13.05	13.02
δ(^{31}P)			0.10	0.31	0.50	0.03
K_{eq}(T_{amb})			1.13	1.52	1.78	1.76

Table 4. ^{13}C NMR Chemical Shifts for Complexes **2a−d**

			2a	2b	2c	2d
δ(^{13}C)	keto (3)	C-2	66.1	66.1	66.2	66.2
		C-5	128.5	129.5	132.1	130.9
		C-6	129.2	128.2	115.6	127.6
		C-4	134.7	136.9	133.4	136.3
		C-7	143.7	132.9	165.7	139.3
		C-3	163.2	162.9	161.8	161.3
		C-1	193.4	193.7	192.1	192.5
	enol (2)	C-2	113.2	113.6	113.4	113.6
		C-5	126.5	126.4	132.1	128.8
		C-6	126.3	128.5	115.6	130.8
		C-4	132.9	135.8	131.9	135.3
		C-7	140.8	130.4	164.1	134.3
		C-3	163.2	162.9	161.8	161.3
		C-1	193.4	193.7	192.1	192.5

attributed to the coordination of the bis(triphenylphosphine)-copper(I) moiety to ligand **1a** through the sulfur atoms. These observations are in agreement with previously reported palladium(II) coordination compounds[8,10] and copper(I) clusters.[21]

The ^{31}P NMR spectrum exhibits a single broad signal centered at δ 0.10. This signal appears at a lower field in comparison to that of the free triphenylphosphine (δ 4.0), confirming the coordination of phosphine to the atom copper.

Even though these ligands have been known since 1910,[22] there are only few examples of transition metal coordination compounds[8−12] where the ligands are bonded through both sulfur atoms in 1,1-dithiolate fashion (Chart 1). To the best of our knowledge, complex **2a** is the first example where this ligand is bonded as a dithio acid resulting in a mononuclear complex instead of polynuclear compounds as reported for sulfur ligand analogues.[13,14]

The syntheses of complexes **2b−d** were carried out using the same procedure. All compounds displayed features similar to those of **2a**. ^{1}H, ^{13}C, and ^{31}P NMR data are given in Tables 3 and 4.

Crystal Structure of Compound 2a. The proposed structure for **2a** was fully established by means of an X-ray diffraction analysis (Figure 1 and Table 5). The metal center is bonded to the ligand through both sulfur atoms in an anisobidentate fashion forming a four-member ring. The central copper atom forms a CuS_2P_2 core with approximately tetrahedral geometry. Geometry distortion arises from the bite S−C−S angle (ca. 73°) and the steric hindrance of triphenylphosphine at P−Cu−P angle (Table 6). This is the coordination mode commonly presented by the dithio acid ligand.[23] The C2−C3, C1−C2, and C3−O bond distances and a strong intramolecular hydrogen bond[24] (Table 7) confirmed that the enol form is the more stable one in the crystal solid state.

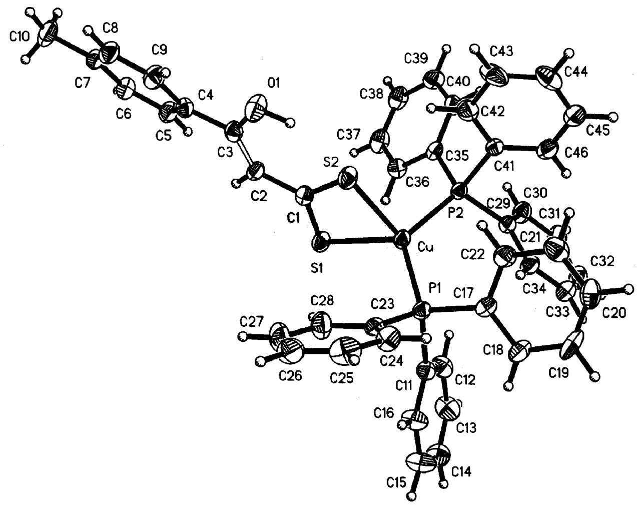

Figure 1.

Table 5. Selected Bond Distances (Å) for **2a**

Cu−P1	2.263(1)	C1−S2	1.707(5)
Cu−P2	2.268(2)	C1−C2	1.448(8)
Cu−S1	2.381(1)	C2−C3	1.366(8)
Cu−S2	2.511(2)	C3−O1	1.338(7)
C1−S1	1.701(6)	C3−C4	1.466(8)

Table 6. Selected Bond Angles (deg) for **2a**

P−Cu−P	123.78(6)	S−Cu−S	73.20(6)
P1−Cu−S1	113.76(6)	P2−Cu−S2	106.16(6)
P1−Cu−S2	109.00(6)	S1−C−S2	117.8(3)
P2−Cu−S1	117.65(5)		

Table 7. Bond Distances (Å) and Angles (deg) of Intramolecular Hydrogen Bonds for **2a**

O−H	0.94(7)	O···S	2.956(5)
S···H	2.08(7)	O−H···S	155(6)

On the other hand, the average Cu−P distances are comparable to those reported in the literature for copper (I)−phospine complexes.[25]

Equilibrium in Solution. In $CDCl_3$, these copper complexes exist in two tautomeric forms, enol (**A**) and keto (**B**) tautomers (Scheme 3), which can be identified on the basis of their NMR spectra (Tables 3 and 4). The NMR spectra of copper(I) complexes **2a−d** have shown characteristic chemical shifts for each tautomeric species. In ^{1}H NMR spectra, the most salient signals for structure **A (**H-8 and H-2**)** were described; vide supra. In all the complexes **2a−d**

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(21) Coucouvanis, D.; Swenson, D.; Baezinger, N. C.; Pedelty, R.; Caffery, M. L.; Kanodia, S. *Inorg. Chem.* **1989**, *28*, 2829.

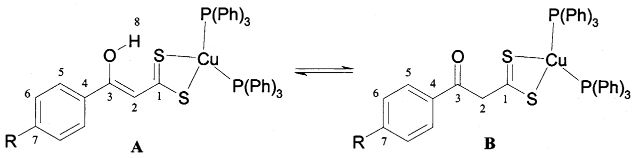
(22) Kelber, C. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1252.

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

(24) (a) Jeffrey, G. A. *An introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997; p 12. (b) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.

(25) (a) Camus, A.; Marsich, N.; Nardin, G. *J. Organomet. Chem.* **1980**, *188*, 389. (b) Nakahodo, T.; Horn, E.; Tiekink, E. R. T. *Acta Crystallogr.* **2000**, *C56*, 1316. (c) Jian, F.; Bei, F.; Lu, X.; Yang, X.; Wang, X.; Razak, I. A.; Raj, S. S. S.; Fun, H.-K. *Acta Crystallogr.* **2000**, *C56*, e288. (d) Deivaraj, T. C.; Vittal, J. J. *Acta Crystallogr.* **2001**, *E57*, m566.

Scheme 3. Tautomeric Equilibrium in Solution



a singlet in the region δ 4.55−4.62 was assigned to the methylene protons H-2 for structure **B**.

Similarly, in the ^{13}C NMR spectra of **2a**−**d**, a signal at δ 66.0 assigned to methylene group C-2 (structure **B)** was observed. Chemical shifts of both dithio acid carbon C-1 and enol carbon C-3 atoms are common for both the forms (Table 4). The tautomeric equilibrium was also confirmed by means of variable-temperature NMR experiments. The intensity relationship of each equilibrium species varies with temperature; at a high temperature the keto tautomer concentration increases, as in acetylacetone derivatives.[23]

To calculate the equilibrium constants for **2a**−**d** compounds, both the enol H-8 and methylene H-2 signals were integrated to determine the population of each tautomer on equilibrium and the methylene integral value was normalized. The value of the tautomeric equilibrium constants were calculated by taking the ratio K_{eq} = [enol]/[keto] (Table 3). In general, K_{eq}'s values reveal that the enol tautomer is the main species in equilibrium and that the electron-withdrawing substituents favor this same tautomer.[26]

It is important to note that ligands **1a**−**d** do not present tautomerism,[2] which may be due to the formation of a formal intramolecular hydrogen bond hence stabilizing the enol species[27] However, their copper(I) complexes have the ability to undergo a keto−enol equilibrium. Thus, we propose that copper(I) coordination reduces the strength of the intramolecular hydrogen bond, prompting the tautomeric equilibrium. Moreover, the shift to lower wavenumbers of ν(C=S) in IR spectrum and the enolic proton signal H-8 shifting upfield in ^{1}H NMR spectrum support this behavior.

Hammett Correlation Studies. In a previous study of free ligands, Larsson and Lawesson observed a linear correlation between NMR chemical shifts of enol protons and Hammett constants.[15] To define the electronic influence of the substituent on the aromatic ring over the coordination centers, ^{13}C NMR was chosen to identify a possible linear correlation with Hammett constants[28] for both ligands **1a**−**d** and complexes **2a**−**d**. As can be seen in Table 8, the substituent displays a cooperative effect in the ligand coordination behavior.

In the ^{13}C NMR spectra of ligands **1a**−**d**, a correlation of the chemical shift for C-3 with Hammett substituent constants was found (eq 1). According to the obtained slope, we deduced that electron-donating substituents decrease electron density that leads C-3 to show carbonyl behavior. Moreover, the acquired slope for eq 2 suggests that electron-donor substituents increase the electron density over C-1 and the donor ability of sulfur is enhanced. This is in agreement with the data reported for the Pd(II) complexes of these ligands.[8,10]

Table 8. Hammett Linear Correlation of δ and $\Delta\delta$ for Compounds **2a**−**d**

atom	eq	*r*	*S*	eq no.
C-3	$\delta = 172.7 - 5.379\sigma$	0.981	0.918	1
C-1	$\delta = 211.1 + 3.886\sigma$	0.930	0.699	2
C-1[a]	$\Delta\delta = -17.9 - 7.531\sigma$	0.986	1.252	3

[a] $\Delta\delta = \delta_{cmpx} - \delta_{lig}$ has been considered.

In the case of copper(I) complexes **2a**−**d** a shielding effect on C-1 ($\Delta\delta$) was observed with respect to the free ligand. A linear correlation of such $\Delta\delta$ was established (eq 3). From the estimated slope, we conclude that electron-withdrawing substituents enhance the shielding effect. However, the increment of the electron density on C-1 in the complexes is opposite to the free ligand behavior (eq 1). This effect could be explained by π back-bonding from the bis(triphenylphosphine)copper(I) fragment to the ligand,[29] and this can also be observed in the IR data for ν(C=S) in the complexes **2a**−**d** (vide supra). To our knowledge, this is the first time where a π back-bonding effect is observed by NMR techniques and Hammett correlation analysis.

Conclusions

Four new mononuclear copper(I) complexes (**2a**−**d**) derived from ligands **1a**−**d** have been synthesized and characterized, and the dithioate-coordination fashion of these ligands is observed for the first time. In solution, complexes **2a**−**d** present keto−enol tautomerism where the enol tautomer was predominant at room temperature and favored by electron-withdrawing groups, as was demonstrated by NMR.

Some linear correlations on ^{13}C NMR data and Hammett substituent constants were found for the ligand (**1a**−**d**) and the complexes (**2a**−**d**), and a shielding effect ($\Delta\delta$) on C1 could be related to a π back-bonding effect. This is the first report of a π back-bonding effect being observed by ^{13}C NMR and Hammett correlation analysis.

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Supporting Information Available: Complete details of the X-ray diffraction study (CIF), an ^{1}H NMR spectrum of complex **2a**, and plots of Hammett correlations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Toullec, J. In *The Chemistry of the Enol*; Rappoport, Z., Ed.; Wiley: Chichester, England, 1990; pp 323−398.

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

(28) May, W. R.; Jones, M. M. *J. Inorg. Nucl. Chem.* **1962**, *24*, 517.

(29) This could be better explained by means of resonance-assisted hydrogen-bonding theory: (a) Steiner, T. *Chem. Commun.* **1998**, 411. (b) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023. (c) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917. (d) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909. (e) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405.