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Characterization of the Coordination Properties of Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II)

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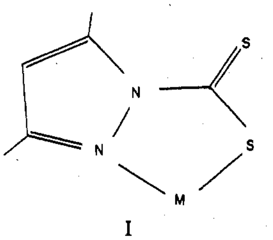
The coordination chemistry of sulfur-containing ligands has attracted a great deal of attention in recent years.[1-4] Our work in this area has centered on the preparation and characterization of the electronic properties of new dithiolate and dithiocarbamate ligands. We have been particularly interested in the design of ligands which promise to induce unusual electronic properties at metal centers. For example, we recently reported the preparation of new dithiocarbamate ligands derived from pyrrole,[5] indoline, indole, carbazole, and imidazole,[6] exploiting a route first outlined by Trofimenko[7] in the preparation of pyrazolecarbodithioates. Our characterization of these ligands and selected transition-metal complexes indicated that each complex contained quite stable MS_4 chromophores, and furthermore, each behaved as a strong-field ligand. Interestingly, Trofimenko suggested that the coordination properties of the ambidentate pyrazolecarbodithioate ligands produced instead N_2S_2 coordination environments. The argument for this chromophore was based mainly on the extra stability associated with a five-membered chelate ring (including the metal) (I) compared to a four-membered ring (II).



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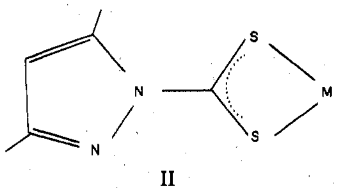


II

Table I. Spin-Hamiltonian Parameters for Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II)

solvent	A_0, G	g_0	$A_\parallel$, G	$g_\parallel$	$A_\perp$,[b] G	$g_\perp$[a]	$g_\perp$[b]	$A_\parallel^N$
$CHCl_3$-DMF	67.7	2.064	171	2.164	16.1	2.014	2.067	16.1
$CHCl_3$-Me_2SO	67.1	2.064	173	2.163	15.2	2.015	2.067	16.3

[a] Calculated from approximations for axially symmetric complexes: $A_0 = (A_\parallel + 2A_\perp)/3$; $g_0 = (g_\parallel + 2g_\perp)/3$. [b] Observed.

In previous cases of ambidentate ligands, where an MS_4 or MN_2S_2 coordination environment was possible, the MS_4 chromophore resulted.[8] Since Trofimenko presented no data to substantiate an N_2S_2 coordination for the title ligand, we felt it necessary to more carefully investigate this system since it led us to develop a new class of compounds.

Experimental Section

Materials. Tetrahydrofuran (THF) and hexanes were dried by standard procedures and distilled immediately before use. Carbon disulfide was dried over Davison 4 Å molecular sieves. Anhydrous copper(II) bromide was obtained from Research Organic/Inorganic Inc. and used without purification, and 3,5-dimethylpyrazole was prepared by a literature method.[9]

Synthesis. Preparation of Potassium 3,5-Dimethylpyrazole-1-carbodithioate. Synthesis of this compound was accomplished by the method of Trofimenko[7] except that THF was used as the solvent, and the reaction was carried out under an argon atmosphere.

Preparation of Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II). To 150 mL of THF were added 2.00 g (9.6 mmol) of the potassium salt of the ligand and 0.992 g (4.4 mmol) of $CuBr_2$ under an argon atmosphere. The resulting red-brown solution was stirred at room temperature for 5 h and filtered to remove KBr. The filtrate was rotary evaporated to a volume of ~75 mL, and hexanes were then added to the point of incipient precipitation. Chilling of this solution at −20 °C for 24 h resulted in the formation of 1.315 g of dark red-brown crystals. Due to the instability of the compound, we were not able to obtain an elemental analysis.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at 27 °C using the Gouy method. Pascal's constants were used to correct the measurements for diamagnetic contributions of the ligands and core electrons of the metal.[10]

Spectroscopic Measurements. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 467 spectrometer. ESR spectra were determined at ~9.0 GHZ employing a Varian E-9 spectrometer coupled to a Hewlett-Packard frequency meter and DPPH as a g-value standard. Visible spectra were obtained in solution in DMF and as a mull in Nujol with a Cary 14 spectrophotometer.

Results and Discussion

The Cu(II) compound of 3,5-dimethylpyrazole-1-carbodithioate is unstable both in the solid state and in solution. It is readily soluble in polar organic solvents such as DMF, Me_2SO, and CH_3CN. The positions of the optical peaks of this compound are identical in the solid state and in solution and are characteristic of a four-coordinate square-planar Cu(II) complex. The infrared spectrum shows identifying absorptions at 1575 cm^{-1} (pyrazole ring), 1340 cm^{-1} (C=S), and 390 cm^{-1} (Cu—S). No absorptions from solvent molecules appear present, precluding a solvated complex.

The copper(II) compound was the metal system chosen to characterize since, in principle, a great deal of information about the nature of the coordination environment can be obtained by the determination of the spin-Hamiltonian parameters from the electron spin resonance (ESR) spectra. These parameters for the copper(II) complex obtained in various solvents are listed in Table I. Much to our surprise, five well-resolved ligand hyperfine lines ($A_\parallel^N$ = 16.1 G) due to two equivalent nitrogen atoms were evident in the glass and solution spectra (see Figure 1). This observation alone characterizes the chromophore as a CuN_2S_2 one. In addition, the values of the principal g value and metal hyperfine coupling

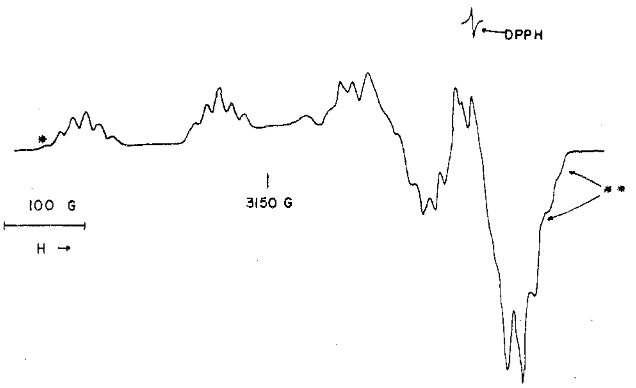
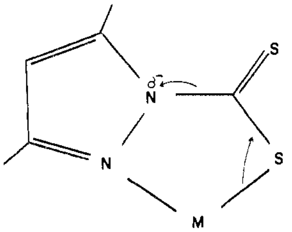


Figure 1. Electron spin resonance spectrum of bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II) in 50:50 $Me_2SO/CHCl_3$ (temperature 100 K; frequency 9.086 GHz). The "extra" (asterisk) weak peak on the low-field side of the $-^3/_2$ parallel line is due to the Cu^{63} isotope effect. The Cu^{63} isotope present also accounts for the two extra peaks on the overshoot line (double asterisk).

constant also support a N_2S_2 environment.[11] The magnitude of the coupling to the nitrogens indicates a very covalent Cu–N bond, something which is quite unusual in the presence of sulfur ligand atoms. For comparison, one can examine the ESR spectra of copper(II) complexes of N_2S_2 Schiff base complexes where the nitrogen constant is significantly less, ranging from 10 to 13 G.[12] The large nitrogen coupling here suggests a particularly important role of the five-member pyrazole ring in the bonding scheme.

The key to unraveling the bonding question lies in the chemistry displayed by the copper(II) complex. We find, as did Trofimenko, that the metal complex of this dithiocarbamate ligand is unstable with respect to loss of CS_2.[7] While the mechanism for this reaction represented below seems logical and as such may be a good indication of the electron density distribution in the complex, it is only speculation on our part; yet it is reasonable that a partial negative charge may reside on the 1-nitrogen.



The result of the extra electron density on the five-membered ring would be to *increase* the donor ability of the nitrogen atom coordinated to the metal atom, thus producing a more covalent metal–nitrogen bond. This effect is most easily seen in the larger unpaired electron density on the nitrogen from the antibonding molecular orbital, which is mainly of copper d character. Since the ligand itself is unstable in the solid state, the decomposition is ligand induced and not metal induced. In some ways, the decomposition in the presence of a metal is the reverse reaction of the well-known CS_2 insertion reaction of metal amides. We investigated the solid-state decomposition of this complex. As CS_2 is lost, the resulting complex is diamagnetic as indicated by the total loss of a detectable ESR signal (in solution), by the decrease in the magnetic moment measured in the solid state, and by the disappearance of C=S (1340 cm^{-1}) and Cu—S (390 cm^{-1}) absorptions in the infrared spectrum. The data we obtained are listed in Table II. We were not able to obtain a compound whose stoichiometry was exactly Cu(pyrazolate)$_2$ by decomposition of the dithiocarbamate. It is possible that a copper(II)–copper(II) dimer or higher aggregate is formed or that a copper(I)–copper(III) complex results. Our data do not allow us to differentiate between these possibilities.

Table II. Magnetic Susceptibility (μ_B)

>1 h	1.85	36 h	1.37
12 h	1.64	2 months	0.79
24 h	1.46		

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Registry No. Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II), 67800-65-1.

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Studies of a 15-Membered Tetraphosphorus Macrocyclic Ligand

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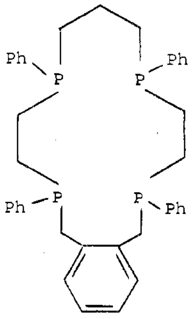
Recently, we reported the synthesis of a novel tetraphosphine macrocyclic ligand, 1,4,8,11-tetraphenyl-13,14-benzo-1,4,8,11-tetraphosphacyclopentadecane, Benzo-15-P_4, having a 15-membered core.[1] Others have also prepared similar tetradentate macrocycles having 16^2- and 14^3-membered cores, but as yet, no physical information dealing with the coordination properties of these ligands has appeared. In lieu of this, we wish to present some data which tend to support our contention that these ligands are of the strong-field variety, possibly comparable to the phthalocyanines.[4]



Benzo-15-P_4

Experimental Section

All UV–vis spectra were recorded on a Cary 15 spectrophotometer using 10^{-3} M solutions in either water, methanol, or chloroform.