

The Interaction of *N*-2-Pyridyl-, *N*-2-Picolyl- and *N*-2-Lutidyl-*N'*-arylthioureas with Copper(II): an Electron Spin Resonance Study

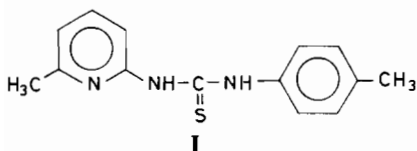
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Electron spin resonance (ESR) spectral studies have been used to characterize copper(II) complexes with different donor atoms [1–3]. Few studies of copper(II) complexes with sulfur donor atoms have appeared [4] because of their relative instability due to reduction to copper(I) species. Recently, to detect transient copper(II) thiolate species, quickly freezing freshly made mixtures of copper(II) thiol solutions has proven successful [4].

Similar instability of copper(II) complexes occurs in the presence of *N*-substituted thioureas [5]. Reported here are the copper(II) ESR parameters for a range of *N*-heterocyclic *N'*-arylthioureas having a potential heterocyclic nitrogen donor as well as the thiocarbonyl sulfur donor. We represent thioureas derived from 2-aminopyridine by 2A, those from the various 2-aminopicolines by 2A3, 2A4, etc. and those from 2-amino-4,6-lutidine by 2A46. The thioureas in which *N'* has a phenyl, *o*-tolyl, *p*-tolyl, or naphthyl function have TU, TU2, TU4 and TUN, respectively, at the end of their symbols. For example, *N*-2-(6)picolyl-*N'*-(*p*-tolyl)thiourea has the symbol 2A6TU4, and represents I.



Experimental

The thioureas were prepared by mixing ethanolic solutions of 2-aminopyridine, one of the 2-aminopicolines, or 2-amino-4,6-lutidine with phenyl, *o*-tolyl, *p*-tolyl or 2-naphthyl isothiocyanate in ethanol. If a solid did not form on stirring for *c.* 0.5 h, gentle refluxing aided the formation of the desired thiourea, which was filtered with suction and washed with cold ethanol. The various thioureas were

dissolved in nonpolar solvents, such as chloroform or methylene chloride, to near saturation. Nearly saturated aqueous solutions of copper(II) chloride were rapidly mixed with the solution of thiourea, resulting in a brown-colored organic layer. A syringe was used to quickly remove a portion of the organic layer and transfer it to an ESR tube which was immediately immersed in liquid nitrogen. The sample tubes were placed in a conventional liquid nitrogen insert Dewar in order to record ESR spectra on a Varian E-4 electron spin resonance spectrometer. All spectra were calibrated using DPPH ($g = 2.0036$). Methylene chloride solutions often gave a more intense signal, but required more rapid freezing.

Results and Discussion

Upon mixing of the aqueous copper(II) chloride solution with the organic layer containing a 2-heterocyclic thiourea, a transient brown color appears, which rapidly gives way to yellow. By rapidly freezing the brown solution, weak copper(II) ESR spectra typical of an approximately axial environment with a $d_{x^2-y^2}$ ground state can be observed (Fig. 1). These signals are consistent with the copper(II) coordination sphere having one or more sulfur atoms, which causes an overlapping of the fourth parallel feature (derived from $M_I = -3/2$) with the more intense perpendicular features. Consequently, these spectra have lower values for g_{\parallel} than has been found for CuN_4 or CuO_4 chromophores [6]. Confirmation of nitrogen coordination is the appearance of nitrogen superhyperfine splitting (*c.* 12 G) on the $M_I = +3/2$ parallel feature in all of the spectra. Therefore, the transient copper(II) species observed are probably CuN_2S_2 chromophores with two thiourea ligands bonding via the heterocyclic nitrogen and thione sulfur atoms. This is consistent with the bonding found for a series of cobalt(II) complexes

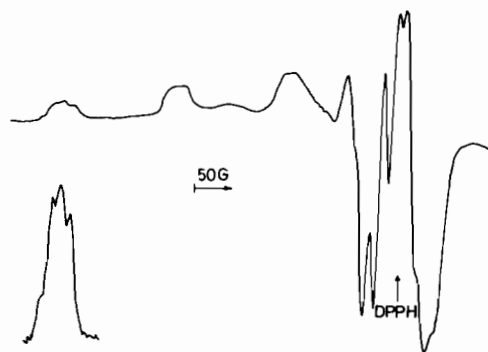


Fig. 1. Frozen solution ESR spectra of a transient copper(II) complex of an *N*-2-heterocyclic *N'*-arylthiourea.

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TABLE 1. ESR parameters of transient bis(pyridyl-, picolyl- and lutidylthiourea)copper(II) ions recorded as frozen chloroform or methylene chloride solutions

Thiourea	A_{\parallel}	A_{\perp}	A_{ave}	g_{\parallel}	g_{\perp}	g_{ave}	Solvent
<i>N'</i> -phenyl thioureas							
2ATU	156	17	63	2.150	2.027	2.068	CHCl ₃
2A3TU	168	14	65	2.168	2.031	2.077	CHCl ₃
2A4TU	156	18	65	2.156	2.032	2.073	CHCl ₃
2A5TU	153	16	62	2.153	2.030	2.071	CHCl ₃
2A6TU ^a							CH ₂ Cl ₂
2A46TU ^a							CHCl ₃ /CH ₂ Cl ₂
<i>N'</i> - <i>o</i> -tolylthioureas							
2ATU2	165	17	66	2.149	2.026	2.067	CHCl ₃
2A3TU2	154	18	63	2.151	2.028	2.069	CHCl ₃
2A4TU2	158	16	63	2.151	2.028	2.069	CHCl ₃
2A5TU2	161	17	65	2.148	2.026	2.067	CHCl ₃
2A6TU2 ^a							CHCl ₃ /CH ₂ Cl ₂
2A46TU2	151			2.117	2.027	2.057	CH ₂ Cl ₂
<i>N'</i> - <i>p</i> -tolylthioureas							
2ATU4	157	17	64	2.151	2.029	2.070	CHCl ₃
2A3TU4	156	12	60	2.184	2.027	2.079	CH ₂ Cl ₂
2A4TU4	156	17	63	2.151	2.031	2.071	CHCl ₃
2A5TU4	159	18	65	2.150	2.025	2.067	CHCl ₃
2A6TU4 ^a							CHCl ₃ /CH ₂ Cl ₂
2A46TU4	123	26	58	2.119	2.027	2.058	CHCl ₃
<i>N'</i> -naphthylthioureas							
2ATUN	164	14	64	2.140	2.030	2.067	CHCl ₃
2A3TUN	146	20	62	2.156	2.043	2.081	CH ₂ Cl ₂
2A4TUN	151	20	64	2.156	2.027	2.070	CHCl ₃
2A5TUN	155	17	63	2.152	2.026	2.068	CHCl ₃
2A6TUN	146	24	65	2.153	2.026	2.068	CHCl ₃
2A46TUN ^a							CHCl ₃ /CH ₂ Cl ₂

^aInsufficient signal.

found for these thioureas [7]. Also, the g_{\parallel} and A_{\parallel} values of the frozen solutions in Table 1 are comparable to those of other CuN₂S₂ complexes [8].

The data in Table 1 show that the presence of a methyl group in the 6-position of the heterocyclic ring (i.e., 2A6- and 2A46-thioureas) makes observation of the ESR signal difficult. Based on the observation that the brown color formed in the organic layer for these species is always less intense upon mixing, we assume that the rate of formation of the complex in these instances is slower. Therefore, the reduction reaction dominates, and for many of these species we do not observe a sufficiently intense signal to evaluate the ESR parameters. However, in a few instances we do observe a copper(II) signal having values of A_{\parallel} and g_{\parallel} which are both lower than for the complexes of the other thioureas in Table 1. Although these signals are very weak so that any nitrogen superhyperfine structure on $M_1 = +3/2$ would probably not be detected due to the low

signal-to-noise ratio, the lowering of both A_{\parallel} and g_{\parallel} suggests a different coordination sphere for the transient copper(II) complex. The $A_{\parallel} = 124 \times 10^{-4}$ cm⁻¹ and $g_{\parallel} = 2.119$ for the copper(II) species formed with *N*-2-(4,6-lutidyl)-*N'*-(*p*-tolyl)thiourea (2A46TU4) are quite comparable to the values of $A_{\parallel} = 125 \times 10^{-4}$ cm⁻¹ and $g_{\parallel} = 2.126$ reported [9] for *N,N*-dimethyl-*N'*-(*p*-tolyl)thiourea copper(II), which has no coordinating nitrogen atoms. Therefore, the species observed with any of 6- or 4,6-substituted heterocyclic ring thioureas may be CuS₄ centers. It has been suggested [3, 4] that the CuS₄ centers with thiourea ligands have a tetrahedral distortion based on their lower values of A_{\parallel} (and higher values of g_{\parallel}) than for CuS₄ centers formed with thiol donor atoms. A tetrahedral distortion certainly is not unexpected for both CuN₂S₂ and CuS₄ centers given the size of these ligands.

The rest of the thiourea complexes seem to have similar spectra although those thioureas having a

3-methyl group on the heterocyclic ring generally have higher g_{ave} and lower A_{ave} values than the complexes of thioureas having unsubstituted rings or ones with methyl groups in the 4- or 5-positions. Possibly, a methyl group in the 3-position hinders the formation of the chelate ring and an aquo or chloro ligand occupies one of the four planar positions.

Plots of $A_{||}$ versus $g_{||}$ for copper(II) centers have been used to suggest the nature of the planar portion of the copper(II) coordination sphere [1–3]. Recently [4] one of these plots, in which $A_{||}$ is expressed as $10^4 A_{||}/\text{cm}^{-1}$, had a line for CuN_2S_2 , but no example complexes. From that plot for CuN_2S_2 centers, a value of $10^4 A_{||}/\text{cm}^{-1}$ of 150 would have $g_{||} = 2.16$. The complexes of the unsubstituted, the 4-methyl- and 5-methyl-heterocyclic ring thioureas having the various rings attached at N' have values of $10^4 A_{||}/\text{cm}^{-1}$ ranging from 150 to 164 (i.e. calculated from data in Table 1) with $g_{||}$ values from 2.156 to 2.149. Therefore, our data are most supportive of the position of the S_2N_2 line previously reported [4].

It has been suggested [4] that CuN_2S_2 and CuO_2S_2 complexes should be able to be differentiated based on the appearance resolved features of $M_1 = 3/2$ for ^{63}Cu and ^{65}Cu in the spectra of the latter. As can be seen from the representative spectrum in Fig. 1, nitrogen superhyperfine is visible on this feature, but features for the two isotopes, as was found for the CuO_2S_2 complex of 2-thiopyridine N-oxide [10], are not resolved.

The 'inner self-redox' mechanism proposed for reduction of copper(II) dithiophosphinates [11, 12] upon crystallization as well as electron transfer on complex formation are possible mechanisms. It should be noted that after fading, the brown color can be reformed with additional shaking. This indicates that $[\text{thiourea}] \gg \gg \gg [\text{Cu}^{2+}]$ in the organic

layer and suggests reduction on complexation. Our experiments do not rule out dimer formation, but the concentration of the copper(II) complexes would be extremely low.

Acknowledgement

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