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The Synthesis and Coordination Chemistry of a New Dithiocarbamate Prepared from Dipyridylaminedithiocarbamate*

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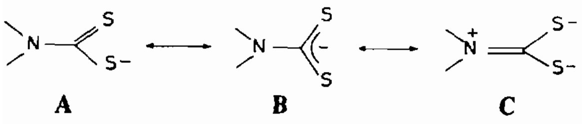
Abstract

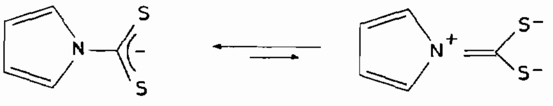
A new dithiocarbamate, dipyridylaminedithiocarbamate (DPADTC), was prepared and the coordination chemistry of this potentially ambidentate ligand was examined. The potassium salt of this new ligand reacts with a variety of MX_2 salts in methanol to yield $M(DPADTC)_2$ complexes. The copper, zinc and cadmium complexes have been isolated and characterized. The physical properties of this new ligand and compounds are discussed. The dithiocarbamate is a weakly coordinating S_2 ligand in the absence of oxygen donor solvents but reverts to a nitrogen donor ligand alone in the presence of such solvents. Insight into the nature of ambidentate coordination in such complexes is offered.

Introduction

The coordination chemistry of sulfur containing ligands has attracted a great deal of recent attention [2–4]. Our work in this area has concentrated on the design and syntheses of new ligands which promise to offer new information on fundamental questions concerning the properties of these systems [5–9]. The interest in dithiocarbamate chemistry has been in the suppression of resonance form C in Scheme 1, an electronic structure typically considered important to the normal coordination properties of dithiocarbamate ligands. We have accomplished this task by the design of the peripheral ligand structure (*i.e.* Scheme 2).



Scheme 1.



Scheme 2.

We have recently become interested in dipyridylamine as a potential source for a new dithiocarbamate. This ligand would offer several interesting features: (i) resonance form C (Scheme 1) could be suppressed because of the electronic and steric effects of the pyridine rings, (ii) the ligand is potentially ambidentate (NS *versus* S_2) in a similar manner to 3,5-dimethylpyrazole dithiocarbamate [10], and (iii) the photochemical, electrochemical, and ESR properties of d6 transition metal complexes of dipyridylamine have recently been thoroughly studied [11]. We were also a little surprised to discover that no report of this ligand existed in light of the availability of the amine. We report here the synthesis of the potassium salt of dipyridylaminedithiocarbamate (DPADTC) and its zinc, cadmium and copper complexes. As in the past, the copper(II) complex has been particularly informative in determining the coordination properties of new ligands.

Experimental

Materials

Dipyridylamine was obtained from Aldrich Chemical Company and was recrystallized from benzene prior to use. Carbon disulfide was obtained from Fisher Scientific Co. and stored over 4 Å molecular sieves prior to use. THF was dried over Na/benzophenone and was distilled prior to use. $CuCl_2 \cdot 2H_2O$ was obtained from J. T. Baker Chemical Co. and was used without further purification. All other chemicals were purchased from Fisher Scientific and used without further purification. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga.

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Preparation of Compounds

K(DPADTC)

5 g (2.92×10^{-2} mol) of dipyridylamine was added to 200 ml of freshly distilled THF containing 1.14 g (2.92×10^{-2} mol) of finely divided potassium under an Ar atmosphere. The solution color immediately turned pale yellow with the evolution of H_2. The mixture was stirred for a 24 h period until all of the potassium had dissolved, leaving a fine yellow precipitate of the potassium salt of dipyridylamine. The reaction mixture was then cooled to –78 °C and 3.5 ml (5.84×10^{-2} mol) of CS_2 was added dropwise; the mixture immediately turned orange The reaction was allowed to proceed for 1 h after which 100 ml of chilled hexanes were added to insure complete precipitation of $DPADTC^-K^+$. The product was collected on a Schlenk frit, washed with cold ether, dried, and stored until needed. Yield 90%, melting point (m.p.) 130 °C dec. *Anal.* Calc. for $C_{11}H_8N_3S_2K{\cdot}2H_2O$: C, 43.54; H, 3.32; N, 13.85; S, 21.13. Found: C, 43.75; H, 3.90; N, 13.85; S, 21.17%. K(DPADTC) is air stable. However, it is very hygroscopic, and all reactions to form metal complexes were carried out without an inert atmosphere.

Zn(DPADTC)₂

The procedure described here was used to prepare all metal complexes of DPADTC. A solution of 0.24 g (1.75×10^{-3} mol) of $ZnCl_2$ in 50 ml of methanol was added dropwise to 1.0 g (3.5×10^{-3} mol) of $DPADTC^-K^+$ in 100 ml of 50/50 methanol/water. A cream colored precipitate formed immediately. The solid was collected, washed with water and dried, yielding 0.90 g (90%) of $Zn(DPADTC)_2$ as a cream colored powder, m.p. >200 °C. *Anal.* Calc. for $ZnC_{22}H_{16}N_6S_4{\cdot}1/2H_2O$: C, 46.60; H, 3.02; N, 14.82. Found: C, 46.53; H, 3.96; N, 15.06%.

Cd(DPADTC)₂

This complex was isolated as described above. It is also a cream colored powder, m.p. >200 °C. *Anal.* Calc. for $CdC_{22}H_{16}N_6S_4{\cdot}31/2H_2O$: C, 39.55; H, 3.46; N, 12.58. Found: C, 39.39; H, 2.93; N, 12.54%.

Cu(DPADTC)₂

This brown powder was isolated as detailed above. No analysis was obtained.

Results and Discussion

A new dithiocarbamate has been prepared. The ^1H NMR of K(DPADTC) in D_2O shows no N–H signal where it was observed for the free amine (9.9 ppm). The ^{13}C NMR does show the very weak $(\mathrm{N{-}C}\begin{smallmatrix}\diagup \mathrm{S}\\ \diagdown \mathrm{S}\end{smallmatrix}(-)$ characteristic carbon signal at 218 ppm indicative of the very long relaxation time for that carbon (pulse interval 30 s). Unfortunately the IR spectrum gives little information on the nature of the C–N bond as has been useful in the past [2, p. 424]. The IR spectrum is simply too complex to attempt to assign any peaks to that vibration.

Both the Zn(II) and Cu(II) DPADTC complexes were prepared and surprisingly both complexes had very poor solubilities in the common range solvents. Neither ^1H or ^{13}C NMR spectra of either complex were reliable.

TABLE I. ESR Data for $Cu(DPADTC)_2$

Solvent	$g_\parallel$	$A_\parallel$[a]	$g_\perp$	$A_\perp$[a]	$A_\perp^N$[a]
DMF/CH_2Cl_2	2.327	154	[b]	[b]	14
Zn matrix	2.109	150	2.046	40	
DMF/CH_2Cl_2[c]	2.43	125	[b]	[b]	

[a] Hyperfine splitting values in units of Gauss. [b] Not resolved. [c] Spectrum obtained after 24 h.

The Cu(II) complex was somewhat more soluble and the ESR spectrum in a frozen glass (DMF/CH_2Cl_2) at 77 K yields as shown in Table I the spin Hamiltonian parameters $g_\parallel = 2.327$, $A_\parallel = 154$ G, $A_\perp^N = 14$ G. The observation of N superhyperfine structure in the perpendicular region of the spectrum clearly indicates that the ligand is coordinated to copper via the pyridine nitrogen. A comparison of the $g_\parallel/A_\parallel$ ratio to those many data compiled by Peisach and Blumberg [12] however, showed that the copper was in an N_2O_2 environment, not an N_2S_2 one. Since any solvent system which gave reasonable solubility properties also contained a possible donor atom, we prepared the copper(II) complex in the zinc(II) matrix (50:1). Here the spin Hamiltonian parameters from the ESR spectrum ($g_\parallel = 2.109$, $A_\parallel = 150$ G, $g_\perp = 2.046$, $A_\perp = 40$ G) were nearly identical to those of the copper(II) complex of diethyldithiocarbamate [13].

Finally, inspection of the frozen glass ESR spectra of solutions of the copper(II) complex at various times up to 24 h after preparation showed a growth of features of a copper O_5 or O_6 environment with a concomitant loss of the N_2O_2 features.

Taken together, these data indicate that DPADTC is a weakly coordinating N donor ligand and a very weakly coordinating S donor ligand. This is clear since (i) in the absence of donor solvent molecules, the Cu complex is in an S_4 environment; (ii) in the presence of oxygen donor solvent molecules, the copper(II) complex is in an N_2O_2 one; and (iii) after time, even this latter complex becomes a $CuO_5(O_6)$ system with the total loss of ligand.

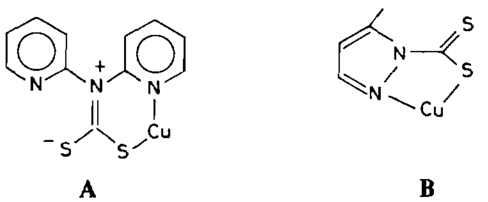

Fig. 1. CuNS coordination by dithiocarbamates.

Several electronic features of the coordination chemistry of DPADTC are also clear: (i) there is apparently little electronic difference between DPADTC and diethyldithiocarbamate, (ii) as a bidentate NS ligand, the apparent extra stability of a six membered chelate ring must be diminished considerably by the positive change build-up on the amine nitrogen (**A**), (Fig. 1). This is in contrast to that observed for 3,5-dimethylpyrazole dithiocarbamate (**B**).

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