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Syntheses and characterization of the palladium(II) and copper(II) complexes of the new 1,1-dithiolate ligand, 1,3-dithiepin-2-carbodithiolate

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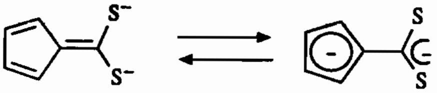
Abstract

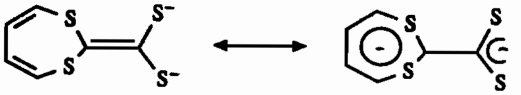
The synthesis of a new 1,1-dithiolate ligand, 1,3-dithiepin-2-carbodithiolate (L^{2-}), has been accomplished from the reaction of carbon disulfide with the lithium salt of 1,3-dithiepin. Copper(II) and palladium(II) complexes of the formula ML_2^{2-} were isolated as the tetraethylammonium salts. Proton nuclear magnetic resonance spectra of the free ligand and the palladium salt suggest a good deal of 'Huckel' aromatic character in the seven membered dithiepin ring. Electron spin resonance spin Hamiltonian parameters obtained from frozen glass samples of the copper(II) complex suggest a highly delocalized four membered chelate ring. Taken together, these data suggest the dithiepin ring is a strong π-acceptor in these complexes.

Introduction

Work in the area of 1,1-dithiolates prior to 1977 yielded an enormous amount of information which has resulted in several comprehensive reviews. However, since then relatively few new samples of 1,1-ethylene dithiolate ligands have been reported. A couple of the more noteworthy systems over the past fifteen years include the cyclopentadiene dithiocarboxylate [1], 1,1-diperfluoro-methyl-2,2-ethylene dithiolate [2] $(CF_3)_2C{=}CS_2^{2-}$, and 1,3-dithiane-2-carbodithiolate [3, 4]. In the first two cases the electronic properties of the ligand greatly influence the overall properties of the transition metal complexes. In the latter case, the potential ligand was only able to be trapped as stable organic derivatives but no transition metal complexes were isolated. This inability to form metal complexes was reasoned to be caused by the lack of resonance stabilization compared to the other ligand systems as suggested for the case of the cyclopentadiene dithiocarboxylate in Scheme 1.



Scheme 1. Resonance structures for cyclopentadiene dithiocarboxylate.



Scheme 2. Resonance structures for 1,3-dithiepin-2-carbodithiolate $(DTDC)^{2-}$.

In this manuscript, we report the synthesis and characterization of a new 1,1-dithiolate ligand which contains the 'tetrathioethylene unit' and has potential aromatic resonance stability as shown in Scheme 2. Very recently, several transition metal complexes of new 1,2-dithiolenes containing the tetrathioethylene unit have been reported [5–8]. This work in large part has been prompted by efforts to incorporate transition metals into the framework of 'organic metals' represented by tetrathiofulvalene (TTF).

The complexes of this ligand with Pd(II) and Cu(II) were prepared and will be discussed. A detailed ^{1}H NMR study of the Pd(II) complex and a semi-empirical MO calculation based on the ESR data of the Cu(II) complex suggest that these systems are in fact quite delocalized, both within the seven membered ring and in the four membered chelate ring.

Experimental

Reagents

Copper(II) chloride and bis(benzonitrile)-palladium(II) chloride were obtained from Aldrich

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Chemical Co. and were used without further purification. 1,3-Dithiepin was prepared by reported procedures and stored at 0 °C under argon [9]. Argon was purchased from Air Products, Inc. Tetrahydrofuran was distilled over sodium/benzophenone under argon prior to use.

Physical measurements

ESR spectra were recorded on a Varian E-3 spectrometer at room temperature and at 100 K. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1}, both as KBr pellets and nujol mulls. NMR spectra were obtained in d_6-DMSO, employing a Bruker WM-250 for 250 MHz ^1H NMR and a JEOL JNM PS-100 for ^{13}C NMR. Electronic spectra were recorded on a Hitachi A-100 spectrophotometer in DMF. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA.

Syntheses

All reactions were carried out under an argon atmosphere employing standard Schlenk techniques unless otherwise stated.

Dilithio-1,3-dithiepin-2-carbodithiolate

n-BuLi (13.0 ml, 2.7 M in hexane) was added to a solution of 1.5 g of 1,3-dithiepin in 250 ml of THF at −70 °C over a 10 min period. This solution was allowed to warm to room temperature slowly over a period of 1 h, then stirred for an additional 6 h. At this time the deep red resolution was cooled to −70 °C and one equivalent of CS_2 (0.7 ml) was added. The solution was allowed to stir for 1 h at −70 °C. The presence of the dianion was confirmed by isolation of dialkylated products [10].

$[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$

To 1.55 g (11.9 mM) of 1,3-dithiepin in 250 ml of dry THF was added 9.17 ml of n-BuLi (2 eq., 2.7 M in hexane) while at −70 °C. The solution was allowed to warm to room temperature and was then stirred for an additional 6 h. The temperature was then lowered to −70 °C and 0.7 ml of CS_2 (1 eq.) was added and allowed to stir at −70 °C for 1 h. At this time 1.15 g of bis(benzonitrile)palladium chloride (0.25 eq.; actually 0.5 eq. based on 50% formation of the dianion) was added and the mixture was allowed to warm to room temperature and stirred for an additional 3 h. The mixture was again cooled to −70 °C, then 1.25 g of tetraethyl ammonium bromide (0.5 eq.) were added and the mixture was allowed to warm to room temperature and stirred overnight. Prior to filtration, 100 ml of absolute alcohol was added and the solution was stirred for 2 h. The product was collected by filtration, washed with alcohol and dried *in vacuo*. Yield 1.5 g, 75%. ^1H NMR δ: 1.15 (24H,t), 3.24 (16H,1), 5.88 (4H,m) 6.14 (4H,m); ^{13}C NMR δ: 7.15, 51.48, 100.61 (C2′), 123.35, 129.26, 178.25 (C2). IR (cm^{-1}): 2990, 2970, 2940, 1550, 1475, 1425, 1390, 1370, 1170, 1020, 1000, 965, 925, 845, 835, 780, 740, 690, 665, 320. *Anal.* Calc. for: C, 43.36; H, 6.19; S, 33.10; N, 3.61. Found: C, 43.30; H, 6.25; S, 33.02; N, 3.57%.

$[N(C_2H_5)_4]_2Cu(C_6H_4S_4)_2$

This compound was prepared in the same manner as above. Yield 75%. IR (cm^{-1}): 3000, 2980, 2940, 1560, 1475, 1450, 1390, 1180, 1170, 1020, 1000, 830, 780, 660, 410, 365. *Anal.* Calc. for: C, 45.90; H, 6.56; S, 35.03; N, 3.82. Found: C, 45.86; H, 6.55; S, 35.09; N, 3.83%.

Results and discussion

Synthesis

The ligand dilithio-1,3-dithiepin-2-carbodithiolate was not isolated, rather an estimation of the amount of dianion present was based on the yields of organic derivatives previously reported [10]. It was assumed that there was 50% dianion present in solution (a slight excess of ligand would not be as detrimental as excess metal salt). Addition of metal salt to the dianion solution resulted in the golden orange solution turning a dark burgundy color. Upon addition of a stoichiometric amount of tetraethylammonium salt, the complex precipitates from solution. Filtration followed by washing with alcohol yielded analytically pure samples. In all cases of isolated metal complexes, IR shows metal–sulfur stretches, at 325 cm^{-1} for Pd–S and at 365 cm^{-1} for Cu–S. However, to date no suitable crystals have been obtained for X-ray analysis.

^1H NMR and ^{13}C NMR

A nuclear magnetic resonance study of $[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$ was undertaken to determine accurate values for the *J*-coupling constants in the dithiepin ring. Since the splitting patterns of these vinylic protons have been used to characterize the electron delocalization in the 1,3-dithiepin moiety [11] it was of interest to determine if in fact this new ligand was stabilized by resonance induced properties as in the case of the cyclopentadiene dithiocarboxylate (Scheme 1).

Values for the four coupling constants (J_{12}, J_{23}, J_{13}, J_{14}) were obtained using the PANIC [12] (Parameter Adjustment in NMR by Interactive Calculation) computer program, which is a minicomputer

TABLE 1. NMR computer input and output data for $[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$

	Input (Hz)	Output (Hz)
W(1)	1536.851	1536.226
W(2)	1472.463	1472.828
$J(1,2)$	11.08	10.724
$J(1,3)$	0.78	0.491
$J(1,4)$	0.78	0.840
$J(2,3)$	8.33	7.993

TABLE 2. Calculated and observed NMR transition of tetraethylammonium bis(1,3-dithiepin-2-carbodithiolate)palladium(II)

Theoretical frequency (Hz)	Intensity	Assigned frequency (Hz)	Frequency difference
1461.293	0.248	1461.492	−0.199
1462.639	0.315	1462.420	0.219
1466.754	1.652	1466.815	−0.061
1469.700	1.417	1469.598	0.102
1470.028	1.505	1469.842	0.186
1474.644	1.735	1474.090	0.554
1475.125	1.685	1475.018	0.107
1478.066	2.365	1478.094	−0.028
1482.186	0.583	1482.586	−0.401
1483.379	0.495	1483.416	−0.038
1525.676	0.495	1525.897	−0.221
1526.868	0.583	1526.776	0.092
1530.988	2.365	1531.219	−0.231
1533.929	1.685	1533.953	−0.024
1534.411	1.735	1534.295	0.115
1539.027	1.505	1539.471	−0.444
1539.354	1.417	1539.715	−0.361
1542.301	1.652	1542.498	−0.197
1546.415	0.315	1545.623	0.792
1547.761	0.248	1548.358	−0.596

version of the LAOCOON [13] type program. Estimates of J values based on the previously reported 1,3-dithiepinyl anion were used to generate a computed spectrum. This calculated spectrum was matched to the experimental one, and the calculation iteratively repeated to convergence according to a least-squares criterion.

The experimental and computer simulated spectra of the palladium complex are essentially identical. The input and output parameters, along with the calculated J values for $[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$ are given in Table 1. Listings of the assigned and calculated lines, along with intensities and errors, are given in Table 2. Table 3 summarizes the NMR parameters for 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin, $[NC_2H_5)_4]_2Pd(C_6H_4S_4)_2$ and the 1,3-dithiepinyl anion.

As can be seen, there is a definite trend in (Δ δ) going from the neutral organo–sulfur compound to the pure dianion. This can best be seen in the increased coupling at the H-5 and 6 positions. It is at these positions where the electron density is increased, hence a shortening of the C-5 and 6 bond, which in turn results in the increased J coupling constant.

The ^{13}C NMR spectrum of the palladium complex shows a fairly substantial shift in the carbon frequencies. Table 4 shows a comparison of the ^{13}C NMR resonances with the previously reported 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin and the known 1,3-dithiepinyl action [10]. There is a much more pronounced polarization of the C2–C2′ double bond in the metal complex in support of a more delocalized π-system in the metal complex.

In an attempt to gain further information of the delocalized nature of these complexes, an ESR study was undertaken. The ESR spectrum of $[N(C_2H_5)_4]_2Cu(C_6H_4S_4)_2$ was obtained in DMF/$CHCl_3$ at room temperature and at 100 K. The hyperfine lines due to ^{63}Cu and ^{65}Cu are resolved in the high field (3/2) transition. The g and A values are given in Table 5.

By analogy to work on $Cu(mnt)_2^{2-}$ [15], $Cu(DDDT)_2^{2-}$ [8] and $Cu(cpdtc)_2^{2-}$ [1], one can assign a ground state $^2B_{1g}[...(xy)^1]$ to the $[N(C_2H_5)_4]_2Cu(C_6H_4S_4)_2$ complex. We confirmed this

TABLE 3. Comparison of ^1H NMR parameters (in Hz) of 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin, $[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$ and the 1,3-dithiepinyl anion

	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin	$[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$	1,3-Dithiepinyl anion [14]
W(1)	1582.293	1536.226	1658.3815
W(2)	1564.737	1472.828	1450.7711
$J(12)$	10.767	10.724	11.08
$J(13)$	0.039	0.491	0.78
$J(14)$	0.620	0.840	0.78
$J(23)$	7.431	7.993	8.33
$\Delta\delta$ (ppm)	0.07	0.25	0.83

TABLE 4. Comparison of ^{13}C NMR (in ppm) frequencies of 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin, $[N(C_2H_5S_4]_2Pd(C_6H_4S_4)_2$ and the 1,3-dithiepinyl anion

	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin	$[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$	1,3-Dithiepinyl anion [14]
C2	155.61	178.25	
C4,7	127.32	129.26	146.7
C5,6	126.59	123.35	121.6
C2′	108.035	100.61	

TABLE 5. ESR parameters for $[N(C_2H_5)_4]_2Cu(C_6H_4S_4)_2$

$\langle g\rangle_0 = 2.0683$	$\langle A\rangle_0 = 76.77\times10^{-4}$ cm^{-1}
$g_\perp = 2.0426$	$A_\perp = 44.54\times10^{-4}$ cm^{-1}
$g_\parallel = 2.0998$	$A_\parallel = 162.56\times10^{-4}$ cm^{-1}

TABLE 7. Electronic spectral data of Pd and Cu complexes of $DTDC^{2-}$ (extinction coefficients)

$[N(C_2H_5)_4]_2Pd(C_6H_4S_4)_2$	$[N(C_2H_5)_4]_2Cu(C_6H_4S_4)_2$
270 (13200)	270 (13130)
290 (9400)	313 (8500)
352.8 (8500)	404 (5400)
384 (7000)	599 (9000)
546 (1500)	

using the equations developed by Maki *et al.* [16] for a $(d_{x-y})^2(d_{xy})^1$ ground state which relate g and A values to the bonding parameters P and K through configurational excitation energies a. The equations take the following form

$$g_{xx} = g_{yy} = 2 - 2\alpha_2 \qquad (1)$$

$$g_{zz} = 2 - 8\alpha_1 \qquad (2)$$

$$A_{xx} = A_{yy} = P[-2 - \alpha_2 - K + 2/7 + 3/7\alpha_2] \qquad (3)$$

$$A_{zz} = P[18\alpha_1 - K - 4/7 - 3/7(2\alpha_2)] \qquad (4)$$

Solving eqns. (1)–(4) for K and P yield values of 0.61 and 0.015 cm^{-1}, respectively. By using the reduction of P from its free ion value ($P_0 = 3.5\times10^{-2}$ cm^{-1}) as a measure of covalency, we calculate the ratio P/P_0, which is a measure of the metal spin density. As can be seen from the P/P_0 value of 0.437 for this copper complex, there is significant delocalization of the electron density in the ground state. This same highly delocalized HOMO has been found for other copper dithiolene complexes and for the copper 1,1-dithiolate of cyclopentadiene dithiocarboxylate. A summary of these results is shown in Table 6.

Determinations of the energies of excited state configurations on the basis of α_1, α_2 and α_3 are not particularly accurate but probably give correct trends. Assuming a spin–orbit coupling constant of −367.6 cm^{-1}, which is lowered from the free ion value of −828 cm^{-1} for Cu(II), to the same extent as P, excitation energy transitions at 339 and 579 nm were predicted. These compare favorably with the experimental values of 404 and 598 nm. The full electronic spectral data for both the copper and palladium complexes are given in Table 7.

The copper and palladium complexes of 1,3-dithiepin-2-carbodithiolate are the first examples of stable transition metal complexes of 1,1-dithiolates which contain the ‘tetrathioethylene unit’. Both the NMR and ESR studies confirm the presence of a delocalized ligand system. The fact that these compounds are air stable (unlike the cyclopentadiene-dithiocarboxylates) will surely generate an interest in this area. This work has aided the efforts to incorporate the TTF type structure into inorganic systems.

TABLE 6. ESR results for some copper 1,1-dithiolates and 1,2-dithiolenes

	g_{iso}[a]	$g_\parallel$[a]	$g_\perp$[a]	A_{iso}[b]	$A_\parallel$[b]	$A_\perp$[b]	P/P_0	K	Reference
$Cu(DTDC)2^{2-}$	2.068	2.0998	2.0426	76.77	162.56	44.54	0.437	0.61	this work
$Cu(Cpdtc)2^{2-}$	2.046	2.094	2.022	85.2	177.1	47.6	0.480	0.59	1
$Cu(DDDT)2^{2-}$	2.069	2.1010	2.0416	68.6	142.3	33.4	0.404	0.555	17
$Cu(mnt)2^{2-}$	2.044	2.082	2.024	72.9	154.5	37.9	0.457	0.555	16
$Cu(dmit)2^{2-}$	2.052	2.099	2.0235	67.0	156.0	35.2	0.450	0.527	18

[a] Standard deviations of g values are 0.001. [b] Hyperfine splitting values in units of cm$^{-1}\times10^{-4}$ with standard deviations of 0.5.

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