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Synthesis of New Thioether Transition Metal Complexes of 2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin and 2-[Bis(ethylthio)methylene]-1,3-dithiepin

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Abstract

Several new Pt(II) and Pd(II) compounds of the type LMX_2 are reported where L can be one of three new organosulfur molecules which contain the tetrathioethylene unit. Those are: 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin (1), 2-(1,5-dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin (2) and 2-[bis(ethylthio)methylene]-1,3-dithiepin (3). Electrochemical characterizations, electronic and infrared studies, and ^1H and ^{13}C spectra are reported for these compounds. In addition, a single crystal X-ray structure was determined for *cis*-2-[bis(ethylthio)methylene]-1,3-dithiepin dichloropalladium(II). This structure belonged to the space group $P2_1/n$ with $a = 9.671(3)$, $b = 16.360(6)$, $c = 10.550(3)$ Å, $\beta = 114.83(2)°$, $V = 1515.8(8)$ Å^3, $\mu_{obs} = 1.90$, and $\mu_{calc} = 1.930$. The structure refined routinely to $R = 3.3$.

Introduction

Partially oxidized compounds containing platinum(II), particularly the tetracyanoplatinates, have attracted considerable attention due to their anisotropic electron transport properties [1–3]. At the same time, there has been an interest in utilizing 'organic metal' components such as TTF in place of CN^- in an effort to blend the features available from the linear chain $Pt(CN)_4{}^{2-}$ species and the organic metals. Siedle and co-workers have reported compounds of the type L_2MX_2 where L is TTF or H_4TTF [4–6]. In an attempt to consider alternatives to these compounds, we have undertaken a synthetic program to consider other molecules containing the tetrathioethylene unit. We report here the preparation and properties of materials of the type $LMCl_2$, where L is a new neutral potentially bidentate organo-sulfur compound which contains the tetrathioethylene unit, which is neither TTF nor a derivative. This paper describes the syntheses and properties of a family of $LMCl_2$ compounds (M = Pd, Pt; L = 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin (1), 2-(1,5-dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin (2) and 2-[bis(ethylthio)methylene]-1,3-dithiepin (3); the crystal structure of one of these, *cis*-2-[bis(ethylthio)methylene]-1,3-dithiepin dichloropalladium(II) has also been obtained. The effect of metal coordination on the NMR and the electrochemistry of the metal complexes and free ligands will also be discussed.

Experimental

Reagents

2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin (1), 2-(1,5-dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin (2) and 2-[bis(ethylthio)methylene]-1,3-dithiepin (3) were prepared as reported [7]. All chemicals were obtained from Aldrich Chemical Co. unless otherwise stated. Acetonitrile was dried according to standard literature procedures.

Physical Measurements

All electrochemical measurements were performed using a BAS CV27. The electrochemical cell used for cyclic voltammetry employed a platinum working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl reference electrode.

Measurements were made on 10^{-3} M solutions of the metal complex with 0.1 M tetrabutylammonium perchlorate serving as the supporting electrolyte. Argon was passed through the solution for fifteen minutes prior to taking the measurements. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1} as both KBr pellets and nujol mulls. Electronic spectra were recorded on a Hitachi A-100 spectrophotometer. NMR spectra were obtained in d_6-DMSO, employing a Bruker WM250 for 250 MHz ^1H NMR and a JEOL JNM PS-100 for ^{13}C NMR. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, Ga.

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Syntheses

2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloroplatinum(II) (4)

A mixture of 0.893 g of K_2PtCl_4 and 0.625 g (1.1 equiv.) of ligand 1 in acetonitrile was refluxed overnight to yield an olive green solid. The crude product was filtered, washed with water, washed with fresh acetonitrile and dried *in vacuo*; yield, 80%. *Anal.* Calc. for $C_8H_8S_4PtCl_2$: C, 19.27; H, 1.61; S, 25.74; Cl, 14.23. Found: C, 19.38; H, 1.64; S, 25.68; Cl, 14.16%. ^{1}H NMR = 3.56 (4H, s), 6.225 (2H, m), 6.40 (2H, m); ^{13}C NMR = 39.98, 107.53 (C2′), 126.37, 127.07, 158.30 (C2). IR (cm^{-1}) = 3050, 3000, 2930, 1570, 1530, 1500, 1415, 1380, 1265, 1130, 1085, 980, 960, 860, 840, 680, 660, 325, 305.

2-(1,5-Dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin dichloroplatinum(II) (5)

This compound was prepared exactly as above using ligand 2. IR (cm^{-1}) = 3040, 2990, 2900, 1560, 1490, 1475, 1450, 1430, 1410, 1360, 1295, 1235, 1205, 1180, 1155, 1135, 1080, 980, 950, 895, 875, 765, 750, 675, 655, 640, 595, 530, 500, 315, 305. *Anal.* Calc. for $C_{14}H_{12}S_4PtCl_2$: C, 29.26; H, 2.09; S, 22.33; Cl, 12.35. Found: C, 29.40; H, 2.12; S, 22.30; Cl, 12.41%.

2-[Bis(ethylthio)methylene]-1,3-dithiepin dichloroplatinum(II) (6)

This compound was prepared exactly as above using ligand 3. IR (cm^{-1}) = 2990, 2960, 2920, 1570, 1500, 1445, 1420, 1400, 1375, 1365, 1270, 1260, 1240, 1170, 1055, 965, 850, 835, 770, 750, 730, 705, 675, 645, 535, 505, 320, 300. *Anal.* Calc. for $C_{10}H_{14}S_4PtCl_2$: C, 22.72; H, 2.65; S, 24.28; Cl, 13.42. Found: C, 22.72; H, 2.7; S, 24.61; Cl, 13.58%.

2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloropalladium(II) (7)

A solution of 0.825 g of bis(benzonitrile) dichloropalladium(II) in 50 ml of acetonitrile was added to 0.625 g (1.25 equiv.) of ligand in 30 ml of the same solvent. The mixture was allowed to stir overnight. The copper colored product was filtered, washed with fresh solvent and dried *in vacuo*; yield, 90%. *Anal.* Calc. for $C_8H_8S_4PdCl_2$: C, 23.45; H, 1.97; S, 31.30; Cl, 17.31. Found: C, 23.61; H, 1.97; S, 31.21; Cl, 17.27%. ^{1}H NMR $\delta = 3.55$ (4H, s), 6.22 (2H, m), 6.38 (2H, m). ^{13}C NMR $\delta = 39.56$, 107.63 (C2′), 126.45, 127.13, 158.29. IR (cm^{-1}) = 3000, 2930, 1570, 1530, 1410, 1385, 1270, 1250, 1140, 1100, 980, 960, 840, 760, 720, 665, 650, 315, 290.

2-(1,5-Dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin dichloropalladium(II) (8)

This compound was made exactly as above using ligand 2. IR (cm^{-1}) = 3040, 3010, 2920, 1560, 1500, 1490, 1450, 1430, 1300, 1235, 1210, 1180, 1160, 1135, 1085, 990, 975, 940, 895, 870, 835, 765, 750, 735, 700, 670, 655, 640, 595, 530, 500, 455, 315, 295. *Anal.* Calc. for $C_{14}H_{12}S_4PdCl_2$: C, 34.60; H, 2.47; S, 26.41; Cl, 14.62. Found: C, 34.87; H, 2.50; S, 26.50; Cl, 14.62%.

2-[Bis(ethylthio)methylene]-1,3-dithiepin dichloropalladium(II) (9)

This compound was prepared exactly as above using ligand 3. IR (cm^{-1}) = 2990, 2960, 2920, 1570, 1500, 1445, 1420, 1400, 1380, 1370, 1270, 1260, 1235, 1170, 1055, 1035, 960, 850, 835, 770, 750, 730, 705, 670, 650, 535, 505, 320, 290. *Anal.* Calc. for $C_{10}H_{14}S_4PdCl_2$: C, 27.30; H, 3.19; S, 29.17; Cl, 16.13. Found: C, 27.31; H, 3.23; S, 29.18; Cl, 16.19%.

Single-Crystal X-ray Analysis

A representative crystal was surveyed and a 1-Å data set (maximum $\sin \theta/\lambda = 0.5$) was collected on a Syntex P1 diffractometer. The diffractometer was equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$ Å). Atomic scattering factors were taken from the International Tables for X-ray Crystallography [8], except hydrogen which was taken from ref. 9 and Pd which was taken from ref. 10. All crystallographic calculations were facilitated by the CRYM system [11]. All diffractometer data were collected at room temperature. Pertinent crystal, data collection, and refinement parameters are shown in Table I.

A trial structure was obtained by direct methods using the heavy atom method. This trial structure refined routinely. Hydrogen positions were calculated wherever possible. The methyl hydrogens were located by difference Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full matrix least-squares refinement contained the scale factor, secondary extinction coefficient, coordinates and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all zero. The final R index was 0.033. A final difference Fourier revealed no missing or misplaced electron density.

The refined structure was plotted using the ORTEP computer program of Johnson [12]. Important distances and angles are given in Table II. See also 'Supplementary Material'.

TABLE I. Single Crystal X-ray Crystallographic Analysis

(a) Crystal parameters	
Formula	$C_{10}H_{14}S_4PdCl_2$ (439.66)
Crystallization medium	acetonitrile
Crystal size (mm)	0.30 × 0.30 × 0.15
Cell dimensions	$a = 9.671(3)$ Å $b = 16.360(6)$ Å $c = 10.550(3)$ Å $\alpha = 90.0°$ $\beta = 114.83(2)°$ $\gamma = 90.0°$ $V = 1515.8(8)$ Å^3
Space group	$P2_1/n$
Molecules/unit cell	4
Density observed (g/cm^3)	1.90
Density calculated (g/cm^3)	1.930
Linear absorption coefficient (cm^{-1})	20.5
(b) Refinement parameters	
No. reflections	1638
Non-zero reflections ($I > 1.0\sigma$)	1552
$R = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma \|F_o\|$	0.033
$G.O.F. = [\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$	1.97
Scale factor	0.896(3)
Secondary extinction coefficient	1.73(7) × 10^{-6}

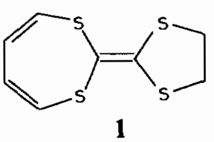
TABLE II. Bond Distances (Å) and Angles (°)

Distances	
Pd–Cl1	2.327(2)
Pd–Cl2	2.304(2)
Pd–S1	2.253(2)
Pd–S2	2.262(2)
S1– 1	1.787(6)
S1– 5	1.792(5)
S2– 6	1.783(6)
S2– 7	1.834(6)
S3– 6	1.759(6)
S3– 9	1.824(7)
S4– 4	1.733(7)
S4– 5	1.744(5)
1– 2	1.308(9)
2– 3	1.469(9)
3– 4	1.325(9)
5– 6	1.340(9)
7– 8	1.512(9)
9– 10	1.502(9)
Angles	
Cl2–Pd–Cl1	93.7(1)
S1–Pd–Cl1	178.1(1)
S2–Pd–Cl1	90.5(1)
S1–Pd–Cl2	86.4(1)
S2–Pd–Cl2	175.1(1)
S2–Pd–S1	89.3(1)
1–S1–Pd	103.3(2)
5–S1–Pd	104.1(2)
5–S1– 1	98.5(3)
6–S2–Pd	104.4(2)
7–S2–Pd	105.4(2)
7–S2– 6	101.7(3)
9–S3– 6	101.3(3)
5–S4– 4	108.1(3)
2– 1–S1	120.4(4)
3– 2– 1	126.6(6)
4– 3– 2	128.8(6)
3– 4–S4	134.1(5)
S4– 5–S1	116.1(4)
6– 5–S1	121.2(4)
6– 5–S4	122.4(4)
S3– 6–S2	116.5(4)
5– 6–S2	120.3(4)
5– 6–S3	123.1(4)
8– 7–S2	114.3(5)
10– 9–S3	113.7(5)

Results and Discussion

Syntheses

The ligands employed in this study (Fig. 1) are particularly interesting since (i) the sulfur atoms should serve as an effective donor site, (ii) the ligand π^* system can backbond with filled metal d orbitals, and (iii) complex formation resulting in the formation of a five-membered 6-π electron ring structure containing the metal, which should have a pronounced effect on the electrochemistry of the tetrathioethylene unit.



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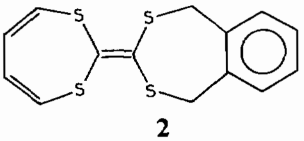

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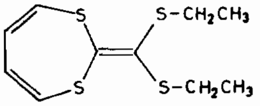

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Fig. 1. Ligand structures: 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin (1); 2-(1,5-dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin (2); 2-[bis(ethylthio)methylene]-1,3-dithiepin (3).

The coordination chemistry of these molecules has yet to be explored. It is known, however, that tetrathiafulvalene (TTF) and tetrahydrotetrathiafulvalene (H_4TTF) (Fig. 2) form complexes with palladium and platinum in which the heterocycle is bonded to the metal through the sulfur atoms [4, 5]. These compounds have a proposed octahedral

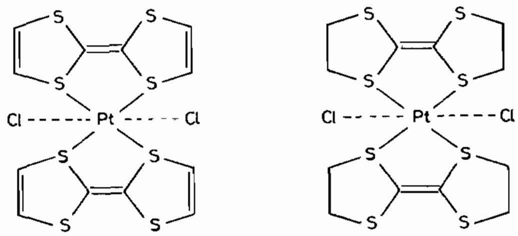

Fig. 2. Proposed structure of metal complexes of TTF and H_4TTF which have M–S bonding.

structure consisting of stacks of TTF containing *trans* MX_2 units between the stacks, resulting in four equatorial sulfurs around the metal and two axial halogen atoms. However, there has been no crystallographic data to support this claim to date.

The platinum compounds described here were obtained by the reaction of K_2PtCl_4 and ligands **1**–**3** in acetonitrile at reflux overnight. The desired $LPtCl_2$ compounds precipitated in analytically pure form. The analogous palladium derivatives were obtained by displacement of benzonitrile from $(PhCN)_2PdCl_2$. The infrared spectrum of all of these compounds shows all major ligand bands present in addition to two M–Cl stretching bands in the range 285–330 cm^{-1} indicating *cis* stereochemistry of the chlorines as reported in earlier work by Siedle *et al.* on similar compounds [6].

Both the platinum and palladium complexes of ligands **2** and **3** exhibited surprisingly poor solubility properties. Therefore, the results of the physical measurements and the overall conclusions will be based exclusively on the analysis of the platinum complexes of ligand **1**.

The electronic spectral data of ligand **1** along with its platinum and palladium complexes are given in Table III. All three ligand bands are present in the metal complexes with only minor shifts in wavelength. In addition d–d transitions are now also present. The long-wavelength absorption in each case can be attributed to a ligand–metal charge transfer band by analogy to metal–TTF complexes reported earlier [5]. In that work, the $(TTF)_2PtCl_2$ ligand–metal charge transfer band appeared at 565 and at 830 nm in the analogous palladium complex. Those values compare to 516 and 714 nm for the Pt and Pd compounds reported here.

Table IV lists the ^1H and ^{13}C NMR data of the platinum and palladium compounds and neutral ligand obtained in d_6-DMSO. As can be seen in both cases little if any perturbations are incorporated into either spectrum upon complexation with the transition metal. This is not so surprising in the ^1H NMR because the protons themselves are somewhat removed from the potential coordination site due to the directional influences of the ring structures. However, in the ^{13}C NMR spectra it was expected that coordination would indeed have an effect on the carbon resonances of the tetrathioethylene unit, hence a change in its polarization. As can be seen in Table IV this again was not the case. All carbon frequencies are basically the same as those in the free ligand.

The metal coordination does, however, invoke a significant effect on the electrochemistry of the

TABLE III. Electronic Spectral Data (nm)

2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloroplatinum(II)	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloropalladium(II)
272 (2792.4)	272 (4764.9)	273 (6436.6)
326 (2594.8)	288 (4023(7)	312 (3078)
354 (1397.2)	344 (1482.4)	358 (1679.1)
516 (199.6)		440 (279.8)
		714 (139.9)

TABLE IV. ^1H NMR and ^{13}C NMR Data (ppm)

	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloroplatinum(II)	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin	2-(1,3-Dithiolan-2-ylidene)-1,3-dithiepin dichloropalladium(II)
H-4,7	6.4071	6.40745	6.40135
H-5,6	6.2309	6.23135	6.21705
$\Delta\delta$	0.1762	0.1761	0.1843
C-2	158.64	158.343	158.291
C-4,7	127.07	127.233	127.133
C-5,6	126.37	126.453	126.450
C-2′	107.53	107.680	107.629

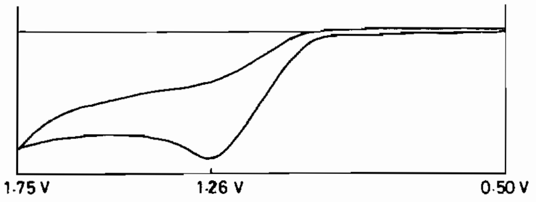

Fig. 3. Cyclic voltammogram for 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin.

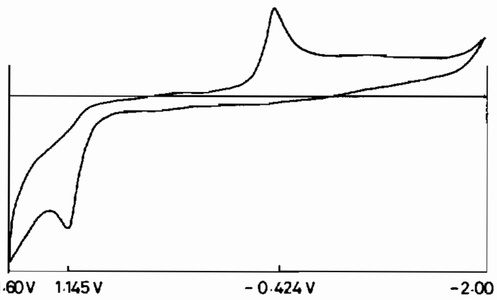

Fig. 4. Cyclic voltammogram for 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin dichloroplatinum(II).

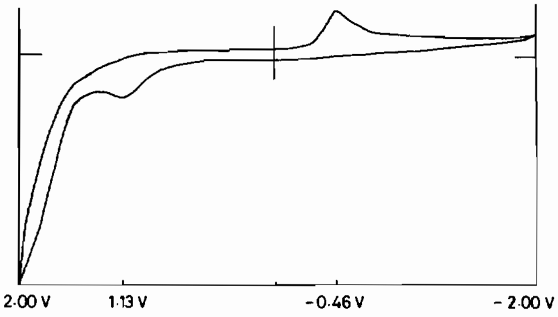

Fig. 5. Cyclic voltammogram for 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin dichloropalladium(II).

complexes. Figures 3, 4, and 5 show the cyclic voltammograms of the free ligand, platinum complex, and the palladium complex, respectively in DMF using tetrabutylammonium perchlorate as the supporting electrolyte. The irreversible oxidation of the ligand has been shown to be a one electron oxidation and is thought to be chemically irreversible. The metal complexes on the other hand have this same oxidation wave, but they also have a reduction wave associated with it. This reduction wave is not present unless one first scans through the oxidation wave. This may be explained as a stabilizing factor of the radical cation initially formed or it may in fact be associated with the ligand–metal charge transfer interaction as postulated by the electronic spectral data.

Conclusions

Characterization of these compounds has relied heavily on analogy on previously reported compounds. Elemental analysis, IR, NMR, UV–Vis, and the electrochemistry help support the claim of complex formation consistent with the empirical formulas. However, there is still concern that these new compounds may in fact be a cocrystallized product instead of a metal–sulfur bonded one. Foı this reason the X-ray crystal structure analysis has been vital in confirming the proposed structures of our new metal complexes.

The single crystal X-ray analysis of *cis*-2[bis(ethylthio)methylene]-1,3-dithiepin dichloropalladium(II) was obtained (see 'Supplementary Material'). A view of the molecule is given in Fig. 6. The structure shows, that indeed these compounds are coordinated through the sulfurs in a *cis* fashion.

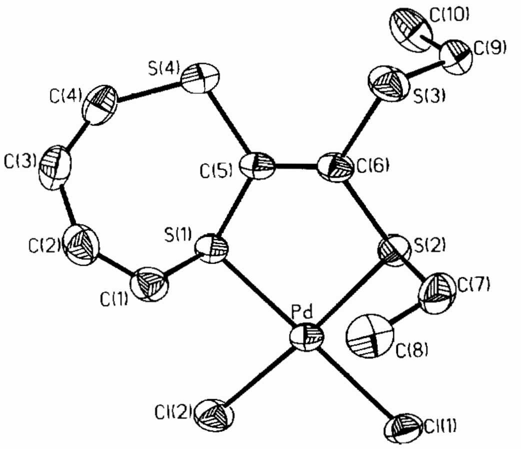

Fig. 6. A view of the molecule.

Supplementary Material

Coordinates for the non-hydrogen atoms, distances and angles, and pertinent crystal and refinement parameters are available from the authors on request.

Acknowledgements

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