

## Metal Tetrathiolenes. 4. Synthesis, Characterization, and Electrochemistry of New Discrete Diplatinum-Tetrathiolene Complexes

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Oxidative addition reactions of low-valent platinum complexes with the "tetrathiolene" (TTL) ligands "tetrathiotetracene" (TTT), "tetrathionaphthalene" (TTN), and "tetrachlorotetrathionaphthalene" (TCTTN) have been investigated. New diplatinum complexes  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  were prepared by reacting  $\text{Pt}(\text{PPh}_3)_4$  with TTL (where  $\text{TTL} = \text{TTT}$ ,  $\text{TTN}$ , and  $\text{TCTTN}$ ). Characterizations of these complexes by chemical and spectroscopic means led to the conclusion that the most probable structure of these complexes involves two metal coordinations bridged by a TTL ligand. The quadridentate bridging nature of tetrathiolene ligands was confirmed by a three-dimensional single-crystal X-ray diffraction study (reported elsewhere) on  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$ . The  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes exhibit unusually rich electrochemistry as established by cyclic voltammetry (in 0.1 M  $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+[\text{ClO}_4]^-$  in  $\text{CH}_2\text{Cl}_2$ ): namely,  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTT})$  oxidizes in two one-electron reversible steps (at ambient temperature) at  $-0.51$  and  $-0.28$  V,  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$  exhibits four reversible one-electron oxidation waves (at ambient temperature) at  $-0.28$ ,  $\sim -0.05$ ,  $\sim 0.01$ , and  $0.31$  V, and  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TCTTN})$  undergoes two reversible one-electron oxidations (at dry ice/acetone temperature) at  $-0.02$  and  $0.21$  V as well as two quasi-reversible waves at  $0.58$  and  $0.94$  V (vs.  $\text{Ag}/0.01$  M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ). These potentials are shifted in the negative direction in comparison to, but can be correlated with, the oxidation potentials of the free tetrathiolene ligands which occur at  $-0.05$  and  $0.44$  V for TTT,  $0.27$  and  $0.65$  V for TTN, and  $0.64$  and  $0.97$  V for TCTTN. This can be taken as an indication that there is a substantial buildup of negative charge on the bridging TTL ligand upon coordination and, conversely, that the oxidation waves involve removal of electron densities from molecular orbitals substantially bridging ligand in character. The unusually rich redox chemistries of the tetrathiolene ligands and complexes are rationalized in terms of molecular orbital energetics.

### Introduction

Metal-dithiolene chemistry was successfully developed and ingeniously exploited by several groups<sup>1-10</sup> during the last two decades. The characteristics of these planar metal-bis(dithiolene) complexes include their extensive  $\pi$ -delocalization and facile redox properties. A recent renewal of interest in this type of transition-metal complex stems from the possibility of producing pseudo-one-dimensional systems which may exhibit highly anisotropic electrical conductivity via columnar stacking of some of these complexes.<sup>11-16</sup>

More recently, several attempts have been made to bridge metal complexes by a quadridentate or a bis-bidentate ligand. These explorations<sup>17-22</sup> have already resulted in a number of elegant synthetic and structural chemistries. Concurrent with these studies, we have chosen the set of ligands tetrathiotetracene (TTT),<sup>23</sup> tetrathionaphthalene (TTN),<sup>24</sup> tetrachlorotetrathionaphthalene (TCTTN)<sup>25</sup> (cf. Chart I), and their selenium analogues as potential ligands for bridging transition-metal complexes to produce a delocalized  $\pi$  system. There are three attractive features which make this class of organic compounds excellent ligands in metal-organic chemistry. First, they are strictly planar with extensive  $\pi$ -electron delocalization. Secondly, each of these molecules has two S-S bonds, one on each side of the molecule, suitable for oxidative addition(s) to low-valent transition-metal complexes. And finally, upon coordinating to two metal complexes, each of these ligands presumably can accommodate up to a total of four (formal) electrons as exemplified in Chart II. The implication of such a qualitative consideration is that the resulting complexes will undergo facile redox reactions. Indeed, the rich electrochemistry of these complexes has been verified experimentally (vide infra). In analogy to the well-known metal-dithiolene systems, these complexes can be named as metal tetrathiolenes (TTL) or metal tetrathienes.

This paper reports the preparation, characterization, and electrochemistry of  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$ , where  $\text{TTL} = \text{TTT}$ ,  $\text{TTN}$ , and  $\text{TCTTN}$ .<sup>26</sup> Since this is the first full account of these new metal-tetrathiolene complexes which behave rather distinctly from the traditional metal dithiolenes, a somewhat detailed discussion on their spectroscopic properties is included for future reference. The unusual stereochemistry of these

Chart I

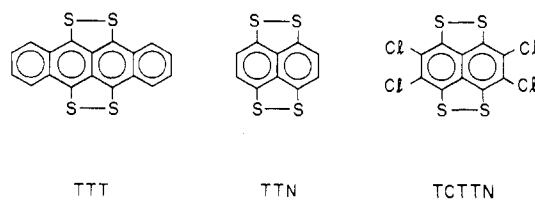
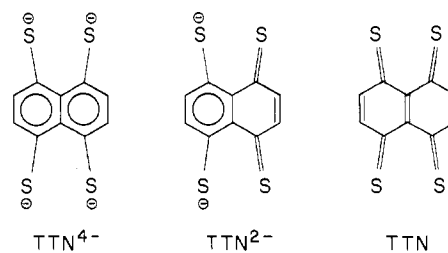


Chart II



metal tetrathiolenes has been established by a complete three-dimensional X-ray structural determination on  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$  reported elsewhere<sup>27</sup> and is found to be consistent with our spectroscopic interpretations. Finally, the electrochemistry of these new materials, as revealed by cyclic voltammetry, provides strong evidence that there is a substantial negative charge buildup on the bridging ligand upon metal coordination.

### Experimental Section

All preparations were performed in an argon-filled Vacuum Atmospheres drybox. Reagent grade benzene, methylene chloride, *N,N*-dimethylformamide (DMF), and acetonitrile were freshly distilled from  $\text{CaH}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{BaO}$ , and  $\text{CaH}_2$ , respectively, under nitrogen. Infrared (IR) spectra ( $4000\text{--}250\text{ cm}^{-1}$ ) were recorded as CsI pellets prepared in the drybox with a Perkin-Elmer Model 467 grating spectrophotometer. UV-vis spectra ( $800\text{--}190\text{ nm}$ ) were recorded in degassed Spectrograde DMF or  $\text{CH}_2\text{Cl}_2$  (Eastman Organic Chemicals) solutions in quartz cells with a Varian Model 634S spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., Bernhardt Microanalytical Laboratories, West Germany, and Midwest Microlab, Indianapolis, Ind. The solubilities of the complexes

to be described herein in common organic solvents were found to be insufficient to allow an accurate determination of the molecular weights by vapor-pressure osmometry (despite several attempts to do so).

The three ligands TTT, TTN, and TCTTN were prepared according to the literature methods.<sup>23-25</sup> The only modifications were vacuum sublimation at 130 °C in the preparation of TTT and Soxhlet extraction using CS<sub>2</sub> and benzene as solvents in the preparation of TCTTN and TTN, respectively. The identity of these compounds was checked by infrared spectroscopy and elemental analysis. Pt(PPh<sub>3</sub>)<sub>4</sub> was purchased from Strem Chemicals.

**Preparation of (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTL), Where TTL = TTT, TTN, and TCTTN.** A mixture of 1.1 mmol (1.37 g) of Pt(PPh<sub>3</sub>)<sub>4</sub> and 0.5 mmol of the TTL ligand (0.176, 0.126, and 0.195 g for TTL = TTT, TTN, and TCTTN, respectively) in 25 mL of benzene was allowed to react under constant stirring overnight. The bright but intensely colored (green, red, and orange for TTL = TTT, TTN, and TCTTN) microcrystalline precipitate, formed while the TTL ligand (dark green, purple-red, and golden yellow for TTL = TTT, TTN, and TCTTN) gradually dissolved, was filtered, washed several times with benzene, and vacuum-dried. Purification was achieved by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN or DMF/CH<sub>3</sub>CN.

Anal. Calcd for (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTT) or C<sub>90</sub>H<sub>68</sub>S<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 60.33; H, 3.83; S, 7.16; P, 6.91; Pt, 21.77. Found: C, 60.31; H, 3.99; S, 7.34; P, 6.71; Pt, 20.81 (by difference).

Anal. Calcd for (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTN) or C<sub>82</sub>H<sub>64</sub>S<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 58.22; H, 3.81; S, 7.58; P, 7.32; Pt, 23.07. Found: C, 57.97; H, 4.02; S, 7.66; P, 7.16; Pt, 23.19 (by difference).

Anal. Calcd for (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TCTTN) or C<sub>82</sub>H<sub>60</sub>S<sub>4</sub>Cl<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 53.83; H, 3.30; S, 7.01; P, 6.77; Cl, 7.75; Pt, 21.33. Found: C, 54.09; H, 3.44; S, 6.96; P, 6.55; Cl, 7.62; Pt, 21.34 (by difference).

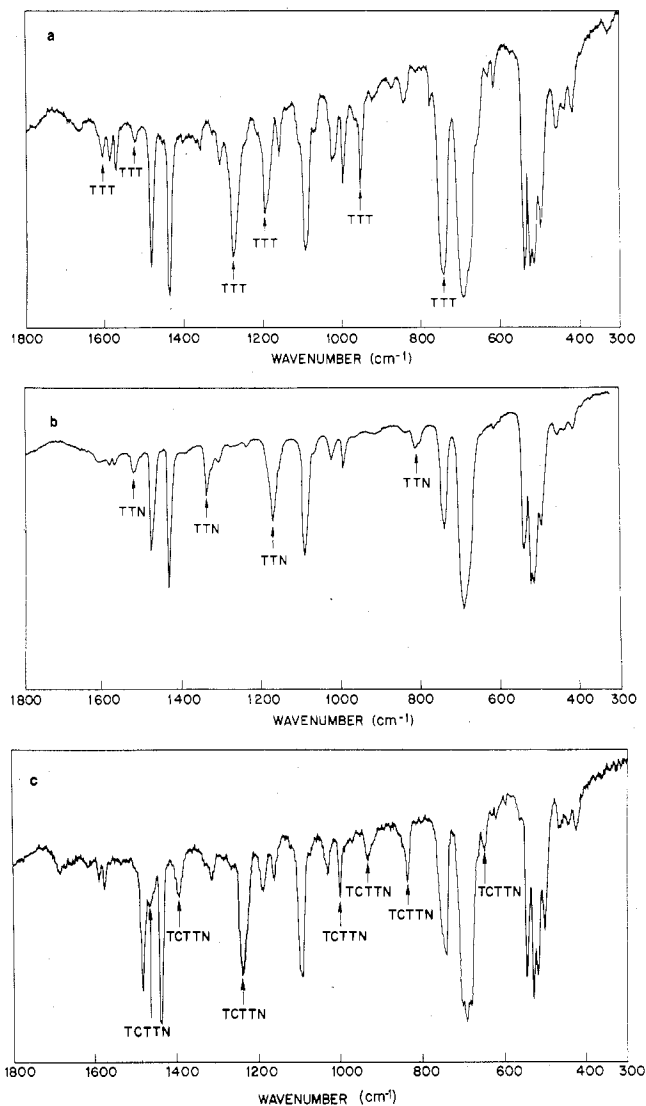
**Cyclic Voltammetry.** The cyclic voltammograms were measured with a Princeton Applied Research (PAR) Model 170 electrochemistry system. The potential was driven by a PAR Model 175 universal programmer.

The three-electrode system consists of a platinum bead as the working electrode, a platinum wire as the counterelectrode, and Ag/0.01 M AgNO<sub>3</sub> in CH<sub>3</sub>CN (separated from the sample solution by a Vycor disk) as the reference electrode. Typical scans with rates of 50–500 mV/s were studied; however, most data quoted here are for the scan rate of 200 mV/s.

All measurements were conducted by using a 10<sup>-3</sup> M solution of the samples in the supporting electrolyte of 0.1 M [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup> (TBAP) in methylene chloride. Polarographic grade TBAP from Southwestern Analytical Chemicals, Austin, Texas, was dried under vacuum at 60 °C overnight whereas the solvent CH<sub>2</sub>Cl<sub>2</sub> was freshly distilled from P<sub>2</sub>O<sub>5</sub>. The samples were loaded in a drybox and the solution was degassed for at least 10 min with solvent-saturated prepurified nitrogen (Matheson Gas Products, East Rutherford, N.J.) before each experiment. The experiments were performed at either ambient or dry ice/acetone temperatures. The solution was stirred between each run to ensure homogeneity. The working platinum electrode was cleaned with a boiling 10% nitric acid solution. The potentials and the peak-to-peak separations were calibrated with known systems.

## Results and Discussions

Bimetallic tetrathiolene complexes of the type (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTL) (where TTL = TTT, TTN, and TCTTN) are obtained essentially quantitatively by reacting 2 mol of Pt(PPh<sub>3</sub>)<sub>4</sub> with 1 mol of the TTL ligands at room temperature for ca. 12 h. The reactions, however, can be accelerated at elevated temperatures. Since the TTL ligands are only sparingly soluble in benzene (as well as most common organic solvents), it is necessary to use a slight excess of the metal complexes to ensure the absence of the TTL ligands in the final product. The excess metal complexes and the released triphenylphosphines can easily be removed by extensive washings with solvents such as benzene. The reactions proceed by gradual dissolution of the TTL crystals (dark green, purple-red, and golden yellow for TTL = TTT, TTN, and TCTTN) to yield an intensely colored solution (dark green, dark red, and orange-red for TTL = TTT, TTN, and TCTTN, respectively) from which the highly colored microcrystalline products eventually precipitate out.

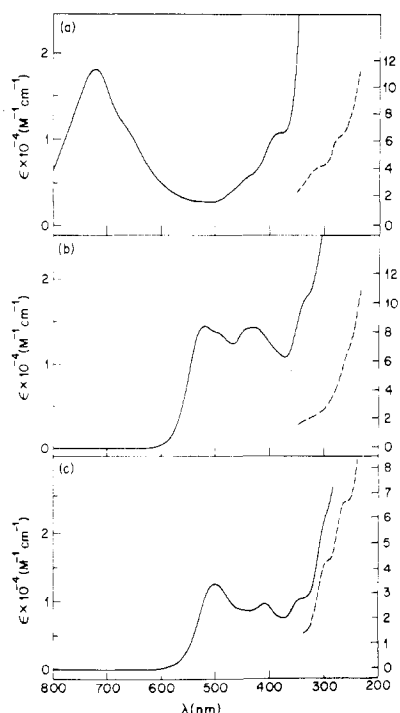


**Figure 1.** Infrared spectra (transmission) of (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTL) in CsI pellets: (a) TTL = TTT; (b) TTL = TTN; (c) TTL = TCTTN. The arrows mark the major TTL bands.

These metal-tetrathiolene complexes are somewhat air-sensitive, especially in solution. They are somewhat soluble in DMF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and 1,2,4-trichlorobenzene, slightly soluble in benzene, and insoluble in acetonitrile, acetone, *n*-hexane, etc. These complexes also exhibit a varying degree of tendency to incorporate solvent molecules in the recrystallization process: e.g., (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTN)·3.55DMF.<sup>27</sup>

The infrared spectra of the (Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(TTL) complexes, depicted in Figure 1a–c for TTL = TTT, TTN, and TCTTN, respectively, revealed the presence of both TTL and Ph<sub>3</sub>P ligands with the former being much weaker in band intensity than the latter due to the 1:4 ratio in number. The coordinated TTL ligands exhibit characteristic infrared bands similar to but somewhat shifted in frequency from that of the free ligands. The extent of such shifts increases along the series TTT  $\lesssim$  TTN < TCTTN which seems to suggest an increasing degree of electronic and/or structural perturbation.

The four strong features in the infrared spectra of the free ligands occur at (a) 1616 (m), (1317 (m), 1304 (s)), 968 (w), and 742 (s) (or 714 (w)) cm<sup>-1</sup> for TTT, (b) 1540 (s), 1362 (s), 1185 (vs), and 797 (vs) cm<sup>-1</sup> for TTN, and (c) 1528 (s), 1428 (s), 1299 (vs), and 854 (m) cm<sup>-1</sup> for TCTTN. By analogy to metal dithiolenes,<sup>28</sup> these four bands can tentatively be assigned as  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{C})$  (ring stretchings),  $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{S})$  (or in-plane C-H bending), and  $\nu(\text{C}-\text{S})$  vibrational



**Figure 2.** Visible-ultraviolet electronic absorption spectra of the  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes in DMF (solid curves) and in  $\text{CH}_2\text{Cl}_2$  (dashed curves) solutions at ambient temperature: TTL = (a) TTT; (b) TTN; (c) TCTTN.

modes. In addition, TTT also exhibits infrared bands at 1519 (w) and 1148 (w)  $\text{cm}^{-1}$  which are probably due to the tetracene rings while TCTTN has bands at 985 (w) and 840 (sh)  $\text{cm}^{-1}$ , some of which are probably due to C-Cl vibrational modes. The bands at 630 (m) and 667 (m)  $\text{cm}^{-1}$  in TTN and TCTTN, respectively, may be due to the asymmetrical combination of the S-S stretches. As shown in Figure 1, most of these features are somewhat shifted when the ligands are coordinated to metal complexes: in  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTT})$  the TTT bands occur at 1609 (w), 1526 (w), 1276 (s), 1194 (m), 954 (w), and 740 (m)  $\text{cm}^{-1}$ ; in  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$  the TTN bands occur at 1530 (w), 1346 (m), 1178 (s), and 818 (w) (808 (sh))  $\text{cm}^{-1}$ ; and in  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TCTTN})$  the TCTTN bands occur at 1465 (w), 1392 (w), 1239 (s), 1000 (w), 931 (w), and 836 (w)  $\text{cm}^{-1}$ . It is apparent that upon coordination, the main  $\nu(\text{C}-\text{C})$  and  $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{S})$  features generally decrease in frequency whereas the  $\nu(\text{C}-\text{S})$  (and  $\nu(\text{C}-\text{Cl})$  in the case of TCTTN) band generally increases in frequency. This is consistent with the notion that upon oxidative addition to the metal complexes, the TTL ligands acquire substantial negative charge (formally reduced) which results in a weakening of the C-C bonds but a strengthening of the C-S bonds (presumably via partial Pt-S  $\pi$  bonding).

The  $\text{Ph}_3\text{P}$  bands appear to be normal. The four strong, highly diagnostic, bands at 539 (s), 523 (s), 514 (s), and 497 (m)  $\text{cm}^{-1}$  are characteristic of a *cis*- $(\text{Ph}_3\text{P})_2\text{Pt}$  arrangement.<sup>29</sup> The Pt-P stretching frequencies (tentatively assigned)<sup>30</sup> are observed at 458 (w), 440 (w), and 420 (w)  $\text{cm}^{-1}$  for  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTT})$ , at 460 (w), 441 (w), and 410 (w)  $\text{cm}^{-1}$  for  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$ , and at 460 (w), 440 (w), and 420 (w)  $\text{cm}^{-1}$  for  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TCTTN})$ .

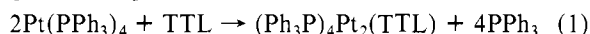
The Pt-S stretching frequency<sup>31</sup> is presumably observable at 328 (w, br)  $\text{cm}^{-1}$  in  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTT})$  but unobservable in the range of 400-250  $\text{cm}^{-1}$  for either  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$  or  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TCTTN})$ .

As shown in Figure 2, the electronic spectra (in DMF except where indicated otherwise) of the dimetal-tetrathiolene complexes exhibit features characteristic of the tetrathiolene

ligands, especially in the visible and near-UV region. In fact, the color of these complexes parallels that of the ligands: TTT, TTN, and TCTTN complexes are generally green, red, and orange, respectively.<sup>23-25</sup>

The visible spectra of the  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes (in DMF solutions) have two major bands with varying degrees of unresolved fine structure at ( $\lambda_{\text{max}}$  in nm with  $\epsilon$  in  $\text{M}^{-1} \text{cm}^{-1}$  in parentheses): (1) 720 ( $1.80 \times 10^4$ ), 652 (sh,  $1.03 \times 10^4$ ), 440 (w, sh,  $5.54 \times 10^3$ ), and 387 (sh,  $1.05 \times 10^4$ ) for TTL = TTT,<sup>32a</sup> (2) 519 ( $1.44 \times 10^4$ ), 490 ( $1.35 \times 10^4$ ), 439 ( $1.43 \times 10^4$ ), and 423 ( $1.43 \times 10^4$ ) for TTL = TTN,<sup>32b</sup> and (3) 502 ( $1.24 \times 10^4$ ), 447 ( $8.50 \times 10^3$ ), and 409 ( $9.44 \times 10^3$ ) for TTL = TCTTN.<sup>32c</sup> These visible bands are, in general, shifted to lower energies in comparison with those of the free ligands which occur at (1) 694 ( $6.39 \times 10^3$ ), 637 ( $4.85 \times 10^3$ ), 583 (sh,  $3.08 \times 10^3$ ), 471 ( $4.85 \times 10^3$ ), 428 (sh,  $2.86 \times 10^3$ ), and 403 (sh,  $1.54 \times 10^3$ ) for TTT (in  $\text{CH}_2\text{Cl}_2$ ), (2) 420 ( $1.84 \times 10^4$ ), 397 (sh,  $1.49 \times 10^4$ ), and 377 (sh,  $8.60 \times 10^3$ ) for TTN (in  $\text{CH}_3\text{CN}$ ), and (3) 423 ( $2.07 \times 10^4$ ), 397 ( $1.58 \times 10^4$ ), and 372 (sh,  $7.23 \times 10^3$ ) for TCTTN (in  $\text{CH}_2\text{Cl}_2$ ). On the basis of intensities and a qualitative molecular orbital calculation<sup>26</sup> on  $(\text{Ph}_3\text{P})_4\text{Pd}_2(\text{TTN})$ , we tentatively assign these visible bands to dipole-allowed transitions such as ligand-to-metal charge transfer (LMCT) and ligand-to-ligand (LL) transitions (here the ligand refers to the TTL bridge). In the UV region, the  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes in  $\text{CH}_2\text{Cl}_2$  solutions exhibit band(s) at (1) 312 ( $4.39 \times 10^4$ ) and 270 (sh,  $6.46 \times 10^4$ ) for TTL = TTT, (2) 336 (sh,  $1.69 \times 10^4$ ) and 260 (sh,  $6.55 \times 10^4$ ) for TTL = TTN, and (3) 340 (sh,  $1.22 \times 10^4$ ), 298 (sh,  $4.27 \times 10^4$ ), and 262 ( $6.70 \times 10^4$ ) for TTL = TCTTN. Some, if not all, of these bands correspond to the UV band(s) of the free ligands which occur at (1) 312 ( $4.85 \times 10^4$ ), 303 (sh,  $3.52 \times 10^4$ ), and 241 ( $3.46 \times 10^4$ ) for TTT (in  $\text{CH}_2\text{Cl}_2$ ), (2) 251 ( $1.46 \times 10^4$ ) for TTN (in  $\text{CH}_3\text{CN}$ ), and (3) 272 ( $3.20 \times 10^4$ ), 261 (sh,  $1.95 \times 10^4$ ), 239 (sh,  $1.86 \times 10^4$ ), and 231 ( $1.97 \times 10^4$ ) for TCTTN (in  $\text{CH}_2\text{Cl}_2$ ).

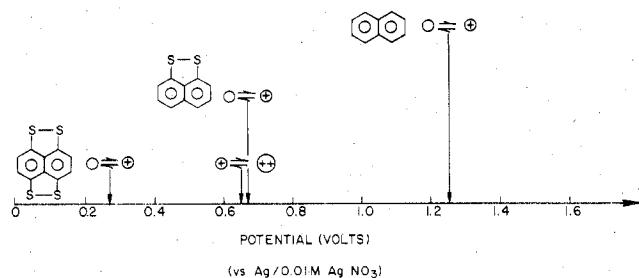
On the basis of these observations it is evident that the reactions between the TTL ligands and the low-valent transition-metal-phosphine complexes proceed readily via oxidative addition(s) of the S-S bond(s) to the metal atoms as depicted in eq 1.



The structure of these  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes probably involves two square-planar-like  $(\text{Ph}_3\text{P})_2\text{Pt}_2\text{S}_2$  coordinations bridged by the approximately planar TTL ligand via cleavage of the two sulfur-sulfur bonds to form four platinum-sulfur bonds. This has been confirmed by a three-dimensional single-crystal X-ray structural study on  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$  (reported elsewhere).<sup>27</sup> The molecule as a whole, though it conforms to the crystallographic  $\bar{1}-i$  site symmetry, is by no means planar. The nonplanar distortion can be characterized by rotations of the platinum coordinations about the S...S edges, resulting in dihedral angles of 38.4°, to give a chair-like configuration. This unexpected molecular distortion can be rationalized in terms of stereochemical constraints imposed by the ligand(s).

**Electrochemistry.** The significance of the  $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$  complexes lies in their unusually rich electrochemistry which is intimately related to the ease of oxidation of the bridging tetrathiolene ligands.

To get an idea why these tetramercapto compounds are prone to oxidation and form stable radical cations, we need only to consider the conversion of naphthalene ( $\text{C}_{10}\text{H}_8$ ) to dithionaphthalene (DTN,  $\text{C}_{10}\text{H}_6\text{S}_2$ ) to tetrathionaphthalene (TTN,  $\text{C}_{10}\text{H}_4\text{S}_4$ ). All three molecules are strictly planar with highly delocalized  $\pi$  systems. However, the character of the highest occupied molecular orbitals (HOMO) in these molecules changes dramatically upon replacement of the hy-

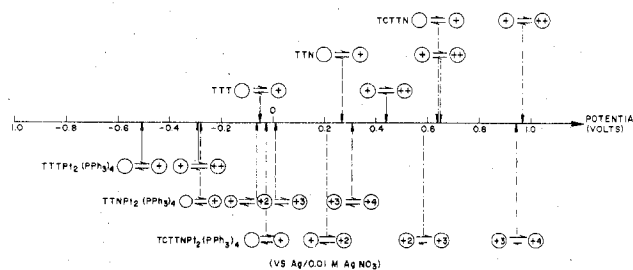


**Figure 3.** Oxidation potentials of naphthalene ( $C_{10}H_8$ ), dithionaphthalene ( $C_{10}H_6S_2$ ), and tetrathionaphthalene ( $C_{10}H_4S_4$ ) vs.  $Ag/0.01 M AgNO_3$ .

drogens at the 1,8 and 4,5 positions, successively, by the sulfur atoms. It goes from a naphthyl ring centered bonding  $\pi$  orbital in  $C_{10}H_8$  to a dithio centered  $\pi$  orbital which is antibonding between the two sulfur atoms in  $C_{10}H_6S_2$  to a tetrathio centered  $\pi$  orbital which is antibonding between the two pairs of sulfur atoms in  $C_{10}H_4S_4$ .<sup>33</sup> As expected, with increasing degree of antibonding, the orbital energies rise substantially in the same direction. This energetic trend then predicts that it should become increasingly easy to oxidize the series  $C_{10}H_{8-n}S_n$  with increasing  $n = 0, 2, \text{ and } 4$  as depicted in Figure 3. In fact a linear relationship has been found between the highest occupied molecular orbital (HOMO) and the first one-electron oxidation potential of  $C_{10}H_{8-n}S_n$ .<sup>33</sup> Furthermore, the fact that the electron(s) come out of orbitals which are highly antibonding between the sulfur atoms for  $C_{10}H_{8-n}S_n$  with  $n = 2$  and 4 suggests that the resulting cations should be quite stable which is indeed the case.

A different variation of these planar organic molecules can be achieved by ring substitution. For example, formal replacements of the four hydrogens in  $C_{10}H_4S_4$  (TTN) by two benzo rings and four chlorines yield  $C_{18}H_8S_4$  (TTT) and  $C_{10}Cl_4S_4$  (TCTTN), respectively (cf. Chart II). These compounds, however, were made by different methods. The redox potentials of these compounds are drastically different. Each molecule exhibits two reversible oxidation and one (or two) irreversible reduction reactions. The first oxidation step occurs at  $-0.05, +0.27, \text{ and } +0.64$  V whereas the second oxidation reaction occurs at  $+0.44, +0.65, \text{ and } +0.97$  V for TTT, TTN, and TCTTN,<sup>34</sup> respectively, as shown in Figure 4. The corresponding irreversible reduction wave occurs at  $-1.30$  (also  $-1.67$ ),  $-1.42$ , and  $-1.26$  V. These values are standardized with respect to  $Ag/0.01 M AgNO_3$ . The trend of the oxidation potentials can be correlated with the electronic effects of the substituents on the naphthalene rings: viz., a formal substitution of the four hydrogen atoms in TTN by four highly electronegative chlorine atoms in TCTTN causes a stabilization of the HOMO(s) which gives rise to an increase in the oxidation potentials, whereas a similar transformation to two benzo groups in TTT causes a destabilization of the HOMO(s) (presumably due to a larger extent of  $\pi$  delocalization), which facilitates the oxidation reaction(s) (i.e., a decrease in the oxidation potentials).

Oxidative additions of these tetrathiolene ligands to two metal complexes produce dramatic changes in the redox behavior of the resulting complexes. Cyclic voltammetry ( $10^{-3} M$  solution in  $0.1 M [(n-C_4H_9)_4N]^+[ClO_4]^-$  in  $CH_2Cl_2$  with a scan rate of  $200 mV/s$ , a Pt bead as the working electrode, a platinum wire as the counterelectrode, and  $Ag/0.01 M AgNO_3$  in  $CH_3CN$  as the reference electrode) revealed two reversible one-electron oxidations at  $-0.51$  and  $-0.28$  V for  $(Ph_3P)_4Pt_2$ (TTT) (at ambient temperature) but four reversible one-electron oxidation waves at  $-0.28, \sim -0.05, \sim 0.01, \text{ and } 0.31$  V for  $(Ph_3P)_4Pt_2$ (TTN) (at ambient temperature). The cyclic voltammogram of  $(Ph_3P)_4Pt_2$ (TCTTN) is more complicated. At dry ice/acetone temperature, it exhibits two



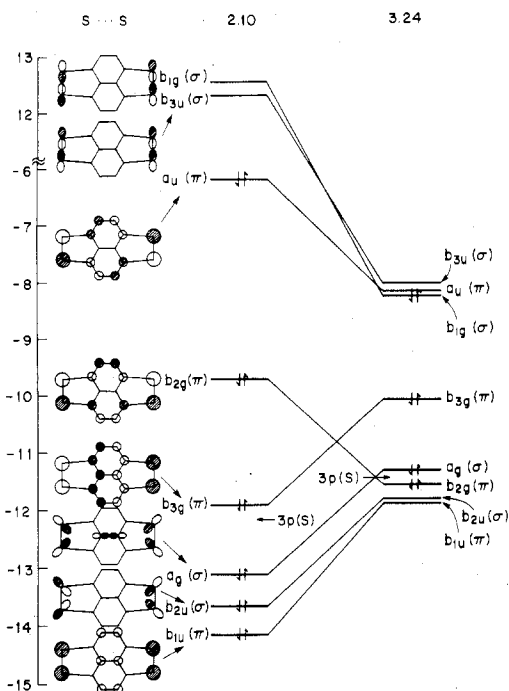
**Figure 4.** Oxidation potentials (vs.  $Ag/0.01 M AgNO_3$ ) of tetra-thiolene ligands TTT, TTN, and TCTTN (top) and diplatinum-tetrathiolene complexes  $(Ph_3P)_4Pt_2$ (TTT),  $(Ph_3P)_4Pt_2$ (TTN), and  $(Ph_3P)_4Pt_2$ (TCTTN) (bottom) as revealed by cyclic voltammetry (sample concentration  $10^{-3} M$ ; supporting electrolyte  $0.1 M [(n-C_4H_9)_4]^+[ClO_4]^-$  in  $CH_2Cl_2$ ; scan rate  $200 mV/s$ ; working electrode Pt bead; counterelectrode Pt wire; reference electrode  $Ag/0.01 M AgNO_3$  in  $CH_3CN$ ).

reversible one-electron oxidations at  $-0.02$  and  $+0.21$  V and two quasi-reversible oxidations at  $+0.58$  and  $+0.94$  V. Two cathodic shoulders inevitably formed upon scanning through the fourth oxidation peak ( $\geq 1.1$  V). At ambient temperature, the first two oxidation waves, though remaining chemically reversible, exhibit complex electron-transfer kinetics which undoubtedly require a more sophisticated technique such as voltammetry with a rotating ring-disk electrode to unravel the mechanistic details. Nevertheless, it behaves like a "reversible" oxidation at  $+0.20$  V with a "reversible" shoulder at  $-0.03$  V. The two quasi-reversible oxidation waves occur at  $+0.64$  and  $+0.97$  V with complex patterns due to subsequent chemical reactions.

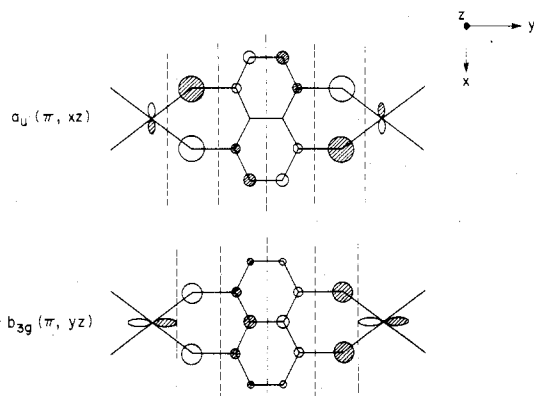
It is of prime importance to note that these oxidation potentials are shifted greatly in the negative direction (more easily oxidized) with respect to the free ligands (vide supra) as depicted in Figure 4. Specifically, the first oxidation potentials of TTT, TTN, and TCTTN decrease by  $-0.46, -0.55, \text{ and } -0.66$  V upon metal complexation to form  $(Ph_3P)_4Pt_2$ (TTT),  $(Ph_3P)_4Pt_2$ (TTN), and  $(Ph_3P)_4Pt_2$ (TCTTN), respectively. This can be taken as an indication of a substantial buildup of negative charge in the bridging TTL ligand upon coordination. Qualitatively, the degree of such negative charge accumulation follows the trend  $TTT < TTN < TCTTN$ . The EPR spectra of the paramagnetic mono- and trications of  $(Ph_3P)_4Pt_2$ (TTN) indicated that in the monocation the spin densities are substantially localized on the TTN ligand with no observable hyperfine interactions(s) with the platinum atoms whereas in the trication there is a significant amount of spin density "localized" on the platinum atom (nonequivalent hyperfine interactions) even though the unpaired electron also resides mainly on the bridging ligand.<sup>26</sup>

In conclusion, the oxidation potentials of the  $(Ph_3P)_4Pt_2$ (TTL) complexes follow the same trend as the free TTL ligands: viz.,  $TTT < TTN < TCTTN$ . The same trend probably holds for the degree of negative charge accumulation on the bridging ligand upon metal complexation.

**Bonding Considerations.** As we pointed out previously,<sup>35</sup> the unusually high charge-buffering ability of the tetrathiolene ligands is qualitatively similar to those of two dithiolenes combined, even though each of the two chelating rings  $C_3S_2$  contains an "odd" number of  $\pi$  orbitals. That is, despite the fact that  $C_3S_2$  moieties of the tetrathiolene ligands are structurally similar to the so-called "odd" dithiolenes such as SacSac which behaves "normally" in Schrauzer's terms,<sup>4b</sup> their redox properties actually resemble those of the so-called "even" dithiolenes such as  $S_2C_2R_2$ , where  $R = CN, CF_3, \text{ etc.}$  The reason is, as depicted in Figure 5,<sup>36</sup> that as the sulfur-sulfur distances in these ligands are increased via oxidative additions to low-valent LUMO-metal complexes, the HOMO  $a_u$  ( $\pi$ ) and the two LUMO's  $b_{3u}$  ( $\sigma$ ) and  $b_{1g}$  ( $\sigma$ ) as well as  $b_{2g}$  ( $\pi$ )



**Figure 5.** Molecular orbital energy diagram<sup>36</sup> for TTN ( $C_{10}H_4S_4$ ) at S-S distances of 2.10 Å (in the free ligand) and 3.24 Å (in the metal complexes). The shaded and empty areas represent schematically the positive and negative lobes of the atomic orbitals. Only orbitals containing substantial sulfur contributions are shown.



**Figure 6.** Schematic representations of the two highest occupied molecular orbitals<sup>36</sup> in bimetallic tetrathiolate complexes (see text and Figure 5 caption).

which are S-S antibonding drop drastically in energy whereas  $b_{3g}(\pi)$  as well as other filled orbitals which are S-S bonding destabilize significantly in energy. Note that only orbitals which are predominantly sulfur in character are depicted in Figure 5. Upon coordinating to the metal atoms,  $b_{3u}(\sigma)$  and  $b_{1g}(\sigma)$  interact strongly with the metal orbitals and are stabilized and fully occupied (resulting in the formal charge of  $TTL^{4-}$ ), leaving  $a_u(\pi)$  and  $b_{3g}(\pi)$  as the two highest occupied orbitals. We believe that the unusually rich electrochemical properties of these metal-tetrathiolene complexes can be related to these energetically high-lying molecular orbitals. In fact, a molecular orbital calculation<sup>36</sup> on  $(Ph_3P)_4Pd_2(C_{10}H_4S_4)$  revealed that the highest occupied orbital of the neutral molecule and the dication are predominantly TTN in character. These two HOMO's, from which one and two electrons are removed to form the mono- and dication, have  $a_u(\pi, xz_-)$  and  $b_{3g}(\pi, yz_+)$  symmetry representations, respectively, as depicted schematically in Figure 6.

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**Registry No.**  $(Ph_3P)_4Pt_2(TTT)$ , 69439-91-4;  $(Ph_3P)_4Pt_2(TTN)$ , 62767-35-5;  $(Ph_3P)_4Pt_2(TCTTN)$ , 69439-92-5;  $Pt(PPh_3)_4$ , 14221-02-4; TTT, 193-44-2; TTN, 35753-06-1; TCTTN, 34588-38-0; naphthalene, 91-20-3; dithionaphthalene, 209-22-3.

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## Stereochemical Changes of N-( $\alpha$ -Phenylethyl)dithiocarbamate Complexes of Cobalt(III)

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By use of one particular enantiomer of the ligand N-( $\alpha$ -phenylethyl)dithiocarbamate (pedtc) the cobalt complexes  $[\text{Co}(\text{pedtc})_3]$  have been prepared in optically active forms. The system shows marked stereoselectivity during synthesis and it has been found that with the (-) ligand,  $\Lambda$ - $[\text{Co}(-)(-\text{pedtc})_3]$  can be isolated in pure form while the (+) ligand yields  $\Delta$ - $[\text{Co}(+)(-\text{pedtc})_3]$ . In nonpolar or weakly polar solvents the configuration of the complex has been found to undergo inversion to the opposite chirality, thus yielding a diastereoisomer which can be isolated in pure form. Reasons for the stereochemical preferences and changes are discussed and related to other systems.

### Introduction

In recent years a good deal of interest has been given to the preparation and stereochemistry of transition-metal complexes of dithiocarbamates.<sup>1-6</sup> Much of this attention has been due to the stereochemical nonrigidity which has been observed for certain of the tris(dithiocarbamate) complexes. The primary modes of investigation have usually involved NMR studies and have centered on stereochemical changes within a mixture of isomers. In most of the cases studied to date, the dithiocarbamate ligands did not themselves possess optical activity and complexes were not isolated in an optically active form.

We have been interested in the use of optically active ligands and have found that stereoselectivity often occurs during the synthesis of certain complexes.<sup>7,8</sup> We wished to examine sulfur-containing ligands as part of our study, and in this paper, we report the preparation, characterization, and stereochemical changes of optically active cobalt(III) complexes containing specific enantiomers of the ligand N-( $\alpha$ -phenylethyl)dithiocarbamate.

### Experimental Section

Optically pure ( $\alpha$ -phenylethyl)amine was obtained from K & K Laboratories and was used without further purification to prepare the dithiocarbamate as the sodium salt. Sodium hydroxide (5.36 g) was dissolved in 30 mL of water, and 8.1 mL of  $\text{CS}_2$  was added. While the solution was stirred vigorously at 0 °C, 15.5 mL of amine was slowly added from a dropping funnel. After stirring of the mixture for 0.5 h, chloroform was used to extract unreacted organic compounds. The aqueous layer was then slowly evaporated to give a solid which was removed by filtration and washed with ether; yield 18.7 g.

The cobalt(III) complexes were prepared by dissolving 0.64 g of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 15 mL of water. The optically active dithiocarbamate (1.0 g) in 10 mL of water was added slowly with stirring. A dark green precipitate gradually formed over a period of 0.5 h. It was removed by filtration and dissolved in methylene chloride, and the solution was extracted twice with water. A solid dark green complex was obtained after evaporation of the organic solvent; yield 0.58 g. Anal. Calcd for  $\text{C}_{27}\text{H}_{30}\text{N}_3\text{S}_6\text{Co}$ : C, 50.06; H, 4.67; N, 6.49; S, 29.69. Found (complex from (-) ligand): C, 49.97; H, 4.73; N, 6.53; S, 29.78. Found (complex from (+) ligand): C, 49.95; H, 4.79; N, 6.51; S, 29.73.

CD spectra were obtained from a Durrum-Jasco ORD-UV-5 spectropolarimeter with CD attachment. Visible absorption spectra were measured on a Cary Model 118 spectrophotometer while NMR

spectra were measured on either a Varian T-60 or HA-100 spectrometer. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

### Results and Discussion

In the preparation of the cobalt complexes  $[\text{Co}(\text{pedtc})_3]$  oxidation of the metal ion occurred upon addition of the metal salt as evidenced by the diamagnetism of the final product. (Such oxidation also has been noted in earlier cobalt preparations.) The use of an optically active dithiocarbamate ligand in synthesis was briefly reported previously.<sup>9</sup> ORD measurements were made on the product but were not related to the stereochemistry of the species.

For tris complexes involving symmetric ligands, two enantiomers ( $\Lambda$  and  $\Delta$ ) are possible and synthesis of these species gives a racemic mixture. When an optically active ligand is used, two diastereoisomers of opposite chirality are possible, e.g.,  $\Lambda(-)(-)(-)$  and  $\Delta(-)(-)(-)$  for the complex from the (-) ligand. These would not be expected to be formed in equal amounts since they possess different properties. Because the species are of opposite overall chiralities, the CD observed in the visible portion of the spectrum should be of opposite sign. Thus, if only a slight predominance of one isomer is formed, a large amount of the CD due to the two species would be canceled, giving rise to a weak resultant CD curve for the mixture. Such an observation was not found, however. With the (-) ligand, the isolated solid gave a very pronounced positive CD band centered at 653 nm. The CD peak is associated with the  $A_{1g} \rightarrow T_{1g}$  absorption band and the magnitude of the peak suggested that a high degree of optical purity was present. In an attempt to determine the relative proportions of each diastereoisomer, thin-layer chromatograms of the solid were developed with a variety of solvents. In all cases, only one band could be observed, suggesting the presence of only one species in the solid. This was confirmed by NMR measurements.

As shown in Table I, it can be seen that the NMR spectrum is also consistent with a single complex and one in which all three ligands are equivalent. No significant broadening was observed for the  $\text{CH}_3$  peaks either at low temperature or under high resolution. These results are consistent with the presence of only one diastereoisomer and one in which all of the ligands