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New Homo- and Heterotrimetallic Thiolato Complexes of Nickel, Palladium, and Platinum. Monomeric and Trimetallic Complexes of Palladium and Zinc with 1,4,8,11-Tetrathiaundecane. Spectral and Solid-State Conductivity Properties of the Trimetallic Compounds

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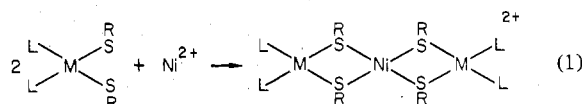
Multimetallic complexes having communication between adjacent metal ions are becoming of increasing interest because of their catalytic and solid-state properties.¹ Of particular interest to us are compounds with different metal ions in specific coordination sites along a short chain. Two ligand types which we have investigated are a substituted phosphinite or secondary phosphite,² and a thiolate.³ The former ligands can be used to prepare mixed-metal complexes having no direct intermetallic communication, but because of the "A-frame" structure found for bridging thiolato complexes it is likely that there is some amount of overlap between the two sets of metal orbitals.

In an earlier article^{3c} we described the preparation of a series of monomeric complexes of type $M(RS)_2L_2$ ($M = Pt, Pd, Ni$). For platinum, monomers were obtained for all monodentate phosphines L , but for palladium and nickel monomeric complexes were formed only with alkyl-substituted phosphines or with chelating phosphines or arsines. We now describe and discuss the use of these monomeric thiolato complexes to synthesize new homo- and heterotrimetallic complexes, and we also extend our coordination chemistry of the ligand 1,4,8,11-tetrathiaundecane to palladium and zinc. Finally, we tabulate and discuss our solid-state conductivity data on a series of trinickel salts.

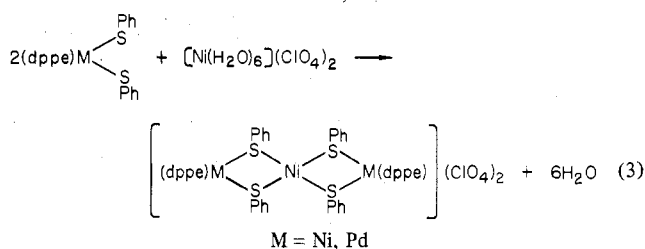
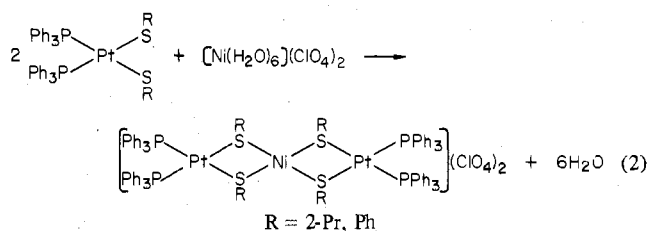
Results and Discussion

In our earlier articles we discussed the synthetic conditions governing the formation and isolation of monomeric thiolato complexes. In every case a nonbridged thiolato complex has lone pairs of electrons on sulfur which can be used to bond to a second metal ion with formation of a bridge bond between the two metal ions.^{3c,4} Indeed it is this mechanism involving substitution of a ligand by a nonbridged coordinated thiolate which leads to the formation of homometallic polymers.^{3b,5} Using this concept of the basicity or nucleophilicity⁶ of a

coordinated nonbridged thiolate, in conjunction with our earlier procedures for the synthesis of monomers, we have found that we have a general route to the synthesis of homo- or heterotrimetallic cations. In this paper we describe a representative group of trimetallic cationic complexes, but it will be apparent that a wide range of choice is available for the end ligands L , and the thiolate substituent R , in the complexes of nickel, palladium, and platinum. In every case we have started with a monomeric bis(thiolato) complex and joined them in pairs by a nickel(II) ion.

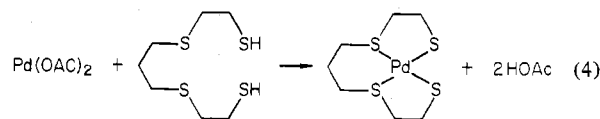


The monomeric complexes which have been used are $Pt(2-PrS)_2(PPh_3)_2$, $Pt(PhS)_2(PPh_3)_2$, $Ni(PhS)_2(dppe)$, and $Pd(PhS)_2(dppe)$.⁷ In each case the reaction with nickel perchlorate occurs rapidly, and brown or blue-gray trimetallic perchlorate complexes are formed (see eq 2 and 3). The



compounds are soluble in dichloromethane solvent but can be isolated by the addition of ethanol or diethyl ether.

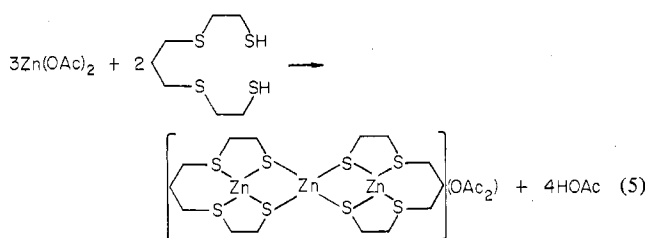
In our previous paper^{3c} we reported the first transition-metal complex of the open-chain thioether-thiolate compound TTU.⁸ This complex was a trimetallic cation obtained from the thiol and nickel fluoroborate, and no changes in experimental conditions would yield the mononickel complex. We have now found that for palladium(II) the monomeric complex is formed. Thus, when palladium(II) acetate is treated with TTU in ethyl acetate or methanol solvent, the monomer precipitates (eq 4). The yellow complex slowly dissolves in chloroform



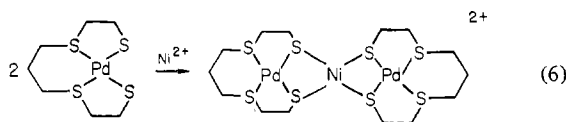
or dichloromethane to give a solution of the same color and can be purified by the slow addition of diethyl ether to this solution. By contrast zinc acetate reacts with TTU in a manner analogous to the nickel(II) reaction. The homotrimetallic complex is formed as the acetate salt (eq 5) as evidenced by a very strong band in the infrared spectrum at 1545 cm^{-1} , a region transparent in the complex $Pd(TTU)$. The trizinc complex reacts with nickel perchlorate to form $[Ni_3(TTU)_2](ClO_4)_2$.

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- (3) (a) Gaines, T.; Roundhill, D. M. *Inorg. Chem.* **1974**, *13*, 2521. (b) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3386. (c) Rauchfuss, T. B.; Shu, J. S.; Roundhill, D. M. *Inorg. Chem.* **1976**, *15*, 2096.
- (4) (a) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 872, 878, 884. (b) Root, C. A.; Busch, D. H. *Ibid.* **1968**, *7*, 789. (c) Lane, R. H.; Pantaleo, N. S.; Farr, J. K.; Coney, W. N.; Newton, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 1610. (d) Fawcett, T. G.; Ou, C.-C.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2058. (e) Chatt, J.; Lloyd, J. P.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 565. (f) Hay, R. W.; Gayler, A. L.; Lawrance, G. A. *Ibid.* **1976**, 939. (g) Hay, R. W.; Lawrance, G. A.; Shone, U. R. *Ibid.* **1976**, 942. (h) de Simone, R. D.; Ontko, T.; Wardman, L.; Blinn, E. L. *Inorg. Chem.* **1975**, *14*, 1313. (i) Dias, A. R.; Green, M. L. *J. Chem. Soc. A* **1971**, 1951. (j) Sato, M.; Green, M. L. *H. J. Organomet. Chem.* **1975**, *94*, 403. (k) Blinn, E. L.; Butler, P.; Chapman, K. M.; Harris, S. *Inorg. Chim. Acta* **1977**, *24*, 139. (l) Ghilardi, L.; Midollini, S.; Sacconi, L. *Ibid.* **1978**, *31*, L431. (m) Issleib, K.; Wienbeck, D. *Z. Anorg. Allg. Chem.* **1978**, *440*, 5.
- (5) (a) Ray, P. C. *J. Chem. Soc.* **1923**, 123, 133. (b) Hofmann, A. W.; Cahows, A. *Ibid.* **1858**, *10*, 320. (c) Hayter, R. G.; Humiec, F. S. *J. Inorg. Nucl. Chem.* **1964**, *26*, 807.
- (6) Busch, D. H.; Jicha, D. C.; Thompson, M. C.; Wrathall, J. W.; Blinn, E. *J. Am. Chem. Soc.* **1964**, *86*, 3642.

- (7) Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane; TTU = 1,4,8,11-tetrathiaundecane.
- (8) (a) Rosen, W.; Bush, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694. (b) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079.



The monomeric complex Pd(TTU) shows the chemistry of a nonbridged thiolato group in its reaction with nickel(II) perchlorate. Addition of nickel perchlorate to a chloroform solution of the complex causes the color of the solution to change to an orange-brown, and isolation of the product gives bis[(1,4,8,11-tetrathiaundecanato)palladium(II)]nickel(II) perchlorate (eq 6).



Far-Infrared Spectra. The far-infrared spectral data in the 300–400 cm^{-1} range are shown in Table I. Additional low-energy bands are present, but from previous spectral assignments for $\nu(\text{M}-\text{SR})$ and $\nu(\text{M}-\text{SR}_2)$ ($\text{M} = \text{Pd}, \text{Pt}$)⁹ we identify the bands in the 300 cm^{-1} region as being primarily metal-sulfur stretching modes. The monomeric compounds, with the exception of the complex $\text{Pt}(2\text{-PrS})_2(\text{PPh}_3)_2$ which has a broad unresolved band, show two absorption bands in this metal-sulfur region. The higher energy one can be assigned to ν_{asym} and the other to ν_{sym} . In separate columns of Table I are listed the frequencies of the platinum and palladium complexes, and it is apparent that there are no major differences in band positions for the two different metals. Furthermore, the addition of a nickel ion to give a heterotrimeric complex also causes no significant change in band position. The bands in the heterotrimeric compounds are still predominantly due to $\nu(\text{Pd}-\text{S})$ or $\nu(\text{Pt}-\text{S})$. We have run spectra for thiolato-nickel(II) monomers^{3c} but can find no absorptions in the 250–400 cm^{-1} range. We therefore conclude that these bands in the heterotrimeric compounds are not due to $\nu(\text{Ni}-\text{S})$ vibrations. The position of ν_{sym} is particularly insensitive to further coordination of the sulfur, and the higher energy band in most cases is too weak to be reliably observed. The complex Pd(TTU) shows a band at 322 cm^{-1} and a further very weak one at 354 cm^{-1} . The higher energy band is broad and is likely a combination of several overlapping ones. Such a situation is to be expected for C_{2v} symmetry about palladium where both thioether and thiolate groups are coordinated to the metal center.

Electronic Spectra. The electronic spectra of the complexes in the visible region are shown in Table II. The spectra have all been measured as solutions in dichloromethane. The higher energy bands are usually shoulders on intense $\pi-\pi^*$ transitions in the UV region, and this makes for a rather imprecise measurement of the extinction coefficient. Nevertheless this does not affect our conclusions since we are making comparisons between complexes having absorptions widely separated in energy from each other.

Monomeric Complexes. The monomeric thiolate complexes of platinum(II) are a yellow color due to a long tail from an intense UV absorption extending into the visible region. From Table II it is apparent that the complexes $\text{Pt}(\text{PhS})_2\text{dppe}$ and $\text{Pt}(2\text{-PrS})_2(\text{PPh}_3)_2$ do not show any electronic bands with λ_{max} at lower energy than 400 nm. In contrast the compounds

$\text{Pd}(\text{PhS})_2\text{dppe}$, $\text{Pd}(\text{SCH}_2\text{CH}_2\text{S})\text{dppe}$, $\text{Ni}(\text{PhS})_2\text{dppe}$, and $\text{Ni}(\text{SCH}_2\text{CH}_2\text{S})\text{dppe}$ show transitions in the 400–550-nm range. The energies of these transitions fall in the sequence of $\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2 > \text{Pd}(\text{PhS})_2\text{dppe} > \text{Ni}(\text{PhS})_2\text{dppe}$. The latter compounds (Table II) show bands at 463 and 427 nm and at 556 and 476 nm, respectively, and from the extinction coefficients ($\sim 10^3$) these bands are assigned to charge-transfer transitions.¹⁰ A reasonable assignment categorizes these bands as the σ and π contributions to the thiolate to metal charge-transfer transitions, and the energy sequence $\text{Pt} > \text{Pd} > \text{Ni}$ is in the expected sequence for the case of reduction of the metal center.¹¹

Multimetallic Complexes. The dimeric complex $[\text{Pd}(\text{es})(\text{PPh}_3)]_2$ crystallizes as deep red crystals which contrasts with the yellow color of the monomeric complex Pd(es)dppe. This red color is not due to additional tailing of the UV band, but it is separate at 500 nm. The extinction coefficient and band position make it very likely that we are dealing with a charge-transfer type transition. It is possible that tertiary substitution on the thiolate by a second metal lowers the energy of the $\text{RS} \rightarrow \text{M}$ transition, but it appears more likely that the transition is in large part due to the Pd–Pd interaction. This communication is made possible because of the A-frame geometry of thiolate dimers, and the interaction causes the nonbonding d_{z^2} orbitals on each palladium to split into a bonding and an antibonding orbital set. This argument is also supported by the data from the thiolato-bridged trimetallic complexes. From the data in Table II a number of trends are apparent. First, the transitions are again of the charge-transfer type, and there is a considerable increase in intensity of bands from the respective monomers. Second, there is a shift to lower energy where the substituent on the thiolate is changed from Ph to 2-Pr. This direction is in agreement with the assignment to a charge-transfer band in the $\text{L} \rightarrow \text{M}$ sense since the increased inductive effect from 2-Pr to sulfur makes the latter easier to oxidize and hence should lower the energy of the $\text{L} \rightarrow \text{M}$ CT band. From Table II, it is apparent that the energy of the electronic transition in the visible region decreases in the sequence $[\{\text{Ni}(\text{PhS})_2\text{dppe}\}_2\text{Ni}]^{2+} > [\{\text{Pd}(\text{PhS})_2\text{dppe}\}_2\text{Ni}]^{2+} > [\{\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2\}_2]^{2+}$. This change is significant in magnitude since the respective band positions are 407, 445, and 543 nm. The transition is of charge-transfer type centered on nickel and follows the expected sequence for the ease of oxidation $\text{Pt}(\text{II}) > \text{Pd}(\text{II}) > \text{Ni}(\text{II})$. The difference in energies between the compounds is significantly greater than that observed for ligand substituent effects (2-Pr vs. Ph), and we believe that this is indicative of charge transfer occurring by direct overlap of the metal orbitals in the folded trimetallic cations. Effects such as these have been recently discussed for the isoelectronic (d^8) rhodium(I) complexes.¹² We do not necessarily propose that these effects lead to significant bond formation since calculations have suggested that the hinging to an “A-frame” geometry does not greatly change the molecular orbital levels or the metal–metal bonding of the square-planar metal centers.¹³ Nevertheless, we believe this intermetallic interaction is sufficient for it to make a contribution to the charge-transfer spectra.

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Table I. Far-Infrared Spectral Data in the Metal-Thiolate Region for the Monomeric and Multimetallic Compounds

complex	$\nu(\text{M-SR}), \text{cm}^{-1}$	complex	$\nu(\text{M-SR}), \text{cm}^{-1}$
$[\text{Pt}(\text{PhS})_2]_n$	322	$[\text{Pd}(\text{PhS})_2]_n$	345
$\text{Pt}(\text{PhS})_2(\text{PMe}_2\text{Ph})_2$	343, 317	$\text{Pd}(\text{PhS})_2(\text{PMe}_2\text{Ph})_2$	337, 322
$\text{Pt}(\text{PhS})_2(\text{diars})$	374, 361	$\text{Pd}(\text{PhS})_2(\text{diars})$	363, 317
$\text{Pt}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_2$	357, 321	$\text{Pd}(\text{PhS})_2(\text{dppe})$	347, 321
$\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2$	336, 324	$\text{Pd}(\text{TTU})$	354, 322
$\text{Pt}(\text{PhS})_2(\text{AsPh}_3)_2$	350, 327	$[\text{Pd}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)]_2$	340, 316
$\text{Pt}(2\text{-PrS})_2(\text{PPh}_3)_2$	321	$[\{\text{Pd}(\text{TTU})\}_2\text{Ni}](\text{ClO}_4)_2$	321
$\text{Pt}(2\text{-PrS})_2(\text{AsPh}_3)_2$	343, 316	$[\{\text{Pd}(\text{PhS})_2(\text{dppe})\}_2\text{Ni}](\text{ClO}_4)_2$	332, 323
$\{\{\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2\}_2\text{Ni}\}(\text{ClO}_4)_2$	324		
$\{\{\text{Pt}(2\text{-PrS})_2(\text{PPh}_3)_2\}_2\text{Ni}\}(\text{ClO}_4)_2$	324		

Table II. Electronic Absorption Bands above 400 nm for the Monomeric and Multimetallic Complexes as Solutions in Dichloromethane

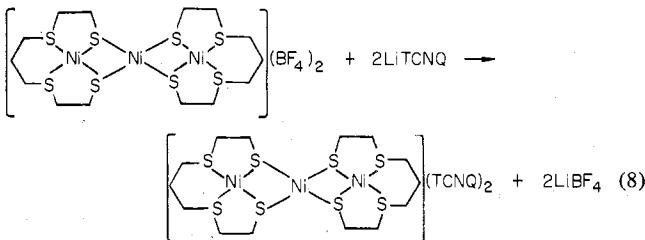
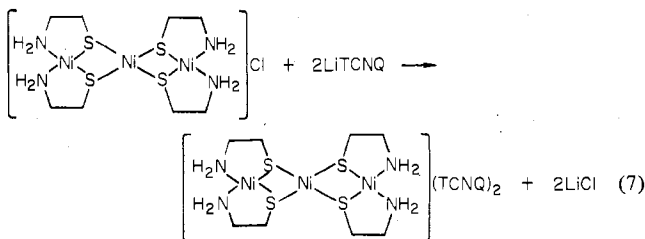
complex	absorption, nm ($\epsilon, \text{cm}^{-1} \text{M}^{-1}$)
$\text{Ni}(\text{SCH}_2\text{CH}_2\text{S})\text{dppe}$	515 (150)
$\text{Ni}(\text{PhS})_2\text{dppe}$	556 (1.1×10^3), 476 (1.3×10^3)
$\text{Pd}(\text{SCH}_2\text{CH}_2\text{S})\text{dppe}$	425 (170)
$\text{Pd}(\text{PhS})_2\text{dppe}$	463 (3.9×10^3), 427 (4×10^3)
$\text{Pt}(2\text{-PrS})_2(\text{PPh}_3)_2$	<400
$\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2$	<400
$[\text{Pd}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)]_2$	500 (450)
$\{\{\text{Ni}(\text{PhS})_2\text{dppe}\}_2\text{Ni}\}(\text{ClO}_4)_2$	407 (2.7×10^4)
$\{\{\text{Pd}(\text{PhS})_2\text{dppe}\}_2\text{Ni}\}(\text{ClO}_4)_2$	445 (2.5×10^4)
$\{\{\text{Pr}(2\text{-PrS})_2(\text{PPh}_3)_2\}_2\text{Ni}\}(\text{ClO}_4)_2$	575 (2.5×10^3)
$\{\{\text{Pt}(\text{PhS})_2(\text{PPh}_3)_2\}_2\text{Ni}\}(\text{ClO}_4)_2$	543 (6×10^2)

Table III. Room-Temperature Compacted Powder Conductivity Data for a Series of Salts of Trimetallic Nickel Cations

complex	conductivity ρ , $\Omega \text{ cm}$
$[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4]\text{Cl}_2$	10^{10}
$[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$	10^{10}
$[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4](\text{TCNQ})_2$	10^8
$[\text{Ni}_3(\text{TTU})_2](\text{TCNQ})_2$	2.8×10^5
$[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4][\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$	10^{10}
$[\text{Ni}_3(\text{TTU})_2][\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$	4×10^9
$[\text{Ni}_3(\text{TTU})_2][\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$	7×10^9
$[\text{Ni}_3(\text{TTU})_2][\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$	10^{10}

Solid-State Data. Two aspects of the chemistry of thiolato-bridged homotrimetallic complexes have led us to investigate whether the materials would behave as semiconductors¹⁴ in the solid state. In our previous paper^{3c} we reported that the complex $[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$ will undergo reduction at the low potential of -300 mV. Since therefore the trinickel cation is easily reducible, there is the possibility that an electron-transfer conductor of the TTF-TCNQ type can be made, providing that the anion and cation can interact intimately in the solid state for electron transfer to occur. This latter condition is possible because of the structural nature of these trimetallic cations. The "A-frame" folding¹⁵ means that the end metal ions have vacant space for the close approach of an anion. Dahl has suggested from calculations that the terminal metal ions in the trimer may interact with Lewis acid type ligands,¹⁶ and the electron withdrawing cyano groups of the tetracyanoquinodimethane anion may allow such interactions in a weak metal-olefin sense of bonding. In principle therefore, the tetracyanoquinodimethane can transfer an electron

to the homotrimetallic cation under the influence of an electrical potential, and if the electron withdrawing cyano groups allow the organic moiety to stack with the cation as a weak π -acid ligand, semiconductor properties may be anticipated. Furthermore, since these trimetallic cations themselves have strong bands in the visible region, we expect the salts to have several available intense absorption bands for visible excitation. The TCNQ^- salts of $[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4]^{2+}$ and $[\text{Ni}_3(\text{TTU})_2]^{2+}$ have been prepared (see eq 7 and 8). Interrante



and others have shown that metal ion complexes of the *cis*-1,2-dicyano-1,2-ethylenedithiolate ligand will act as semiconductors,¹⁷ and we have also prepared the salts of $[\text{Ni}_3(\text{TTU})_2]^{2+}$ with $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$, $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$, and $[\text{Fe}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$ by mixing acetonitrile solutions of the ions in stoichiometric amounts. From Table III it is apparent that the compound $[\text{Ni}_3(\text{TTU})_2](\text{TCNQ})_2$ is a semiconductor. The fluoroborate salt is an insulator, as are the salts with the *cis*-1,2-dicyano-1,2-ethylenedithiolate complexes. Interestingly, the TCNQ salt with $[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4]^{2+}$ shows insulator properties. The materials are noncrystalline powders, and single crystal work will be necessary to distinguish any structural differences between the TCNQ salts of $[\text{Ni}_3(\text{TTU})_2]^{2+}$ and $[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4]^{2+}$, but the failure of the latter to function as a semiconductor may be due to the TCNQ anion forming a hydrogen bond to the terminal amino groups, thereby keeping the ions separated from direct metal-TCNQ orbital overlap.

Experimental Section

Benzenethiol and 2-propanethiol were commercial samples and used without prior purification. 1,4,8,11-Tetrathiaundecane was prepared as described previously.^{3c} Microanalyses were carried out by Galbraith Laboratories, Inc. Tetracyanoquinodimethane was a commercial sample, and the lithium salt was prepared by published procedure.¹⁸

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Disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate and the metal complexes were prepared by published methods.¹⁹ Far-infrared spectra were measured on a Hitachi Perkin-Elmer FIS 3 spectrometer. The samples were ground dry and then made into a mull with Vaseline. The mull was smoothed onto a polyethylene plate which was mounted in the sample beam. Electronic spectra were obtained on a Cary 14 spectrometer with solution samples in 1-cm cells. Peak positions are observed maxima with no line fitting. Melting points on a Fisher-Johns apparatus are uncorrected.

Bis(2-propanethiolato)bis(triphenylphosphine)platinum(II), Pt(2-PrS)₂(PPh₃)₂. To a suspension of *cis*-PtCl₂(PPh₃)₂ (208 mg) in dichloromethane (10 mL) was added 2-propanethiol (0.1 mL) and triethylamine (0.1 mL). Immediately the reaction mixture changed color, and a yellow solution was obtained. The solution was filtered to remove any precipitated Et₃N·HCl, and the volume of the solution reduced to 3-4 mL on a rotary evaporator. Diethyl ether was slowly added to the solution when the complex precipitated. The yellow compound was filtered, washed sequentially with water (to remove any remaining Et₃N·HCl), ethanol, and diethyl ether, and dried in vacuo: yield 115 mg (50%); mp 129-131 °C. Anal. Calcd for C₄₂H₄₄P₂PtS₂: C, 58.0; H, 5.10; S, 7.37. Found: C, 58.2; H, 5.39; S, 7.46. As an alternative to using triethylamine, we have used hydroxide washed Dowex I-8 ion-exchange resin. The reaction proceeds more slowly, but high purity product is obtained. The complex can be recrystallized by dissolution in the minimum volume of chloroform followed by the slow addition of the solution to diethyl ether. ¹H NMR data: δ 1.34 (CH₃, ³J = 7 Hz), δ 4.21 (CH, m).

Bis(2-propanethiolato)bis(triphenylarsine)platinum(II), Pt(2-PrS)₂(AsPh₃)₂. With an analogous procedure, the triphenylarsine complex was prepared; mp 102-104 °C. Anal. Calcd for C₄₂H₄₄As₂PtS₂: C, 52.7; H, 4.63. Found: C, 52.8; H, 5.01.

Bis[bis(2-propanethiolato)bis(triphenylphosphine)platinum(II)]nickel(II) Perchlorate, [[Pt(2-PrS)₂(PPh₃)₂]₂Ni](ClO₄)₂. To a solution of Pt(2-PrS)₂(PPh₃)₂ (189 mg) in dichloromethane (5 mL) was added nickel perchlorate [Ni(H₂O)₆](ClO₄)₂ (74 mg) in acetonitrile (5 mL). The color of the solution changed from yellow to blue. The volume was reduced to 1-2 mL on a rotary evaporator. Ethanol (~1 mL) was added, and then diethyl ether was slowly added until the complex began to precipitate. The complex was filtered, washed with diethyl ether, and dried in vacuo; yield 182 mg (42%). Anal. Calcd for C₈₄H₈₈Cl₂NiO₈P₄Pt₂S₄: C, 50.5; H, 4.44; S, 6.42. Found: C, 50.2; H, 4.60; S, 6.16. The compound melts with decomposition to a red liquid at 235-240 °C. The compound gives a blue solution in acetonitrile, acetone, and ethanol. ¹H NMR data: δ 1.25 (CH₃, d).

Bis[bis(thiophenolato)bis(triphenylphosphine)platinum(II)]nickel(II) Perchlorate, [[Pt(PhS)₂(PPh₃)₂]₂Ni](ClO₄)₂. To a solution of Pt(PhS)₂(PPh₃)₂ (86 mg) in dichloromethane (5 mL) was added [Ni(H₂O)₆](ClO₄)₂ in acetonitrile (~5 mL). The mixture was stirred for 30 min. The volume of solution was reduced and ethanol (2-3 mL) added. Slow addition of diethyl ether gave the complex as a brown precipitate; yield 43 mg. Anal. Calcd for C₉₆H₈₀Cl₂NiO₈P₄Pt₂S₄: C, 54.0; H, 3.78; S, 6.01. Found: C, 53.4; H, 4.00; S, 5.54.

Bis[bis(thiophenolato)[1,2-bis(diphenylphosphino)ethane]palladium(II)]nickel(II) Perchlorate, [[Pd(PhS)₂dppe]₂Ni](ClO₄)₂. With a similar procedure the complex was obtained as brown crystals. Anal. Calcd for C₇₆H₆₈Cl₂NiO₈Pd₂P₄S₄: C, 53.6; H, 4.02. Found: C, 53.1; H, 4.20.

Bis[bis(thiophenolato)[1,2-bis(diphenylphosphino)ethane]nickel(II)]nickel(II) Perchlorate, [[Ni(PhS)₂dppe]₂Ni](ClO₄)₂. Again by use of a similar procedure the complex was obtained as a red-brown solid. Anal. Calcd for C₇₆H₆₈Cl₂Ni₂O₈P₄S₄: C, 56.7; H, 4.26; S, 7.97. Found: C, 55.8; H, 4.07; S, 8.38.

(1,4,8,11-Tetrathiaundecanato)palladium(II), Pd(TTU). To a solution of 1,4,8,11-tetrathiaundecane (TTU) (438 mg) in ethyl acetate (~10 mL) was added a suspension of palladium acetate (401 mg) in ethyl acetate (~10 mL). A yellow precipitate formed. After the solution was stirred for 2 h, the solid was filtered, washed with diethyl ether, and dried in vacuo: yield quantitative; mp 200-205 °C dec. Anal. Calcd for C₇H₁₄PdS₄: C, 25.3; H, 4.24. Found: C, 25.2; H, 4.21. The complex can be purified by dissolution in the minimum volume of chloroform, followed by precipitation with a small quantity

of ethanol followed by diethyl ether.

Bis[(1,4,8,11-tetrathiaundecanato)palladium(II)]nickel(II) Perchlorate, [[Pd(TTU)₂Ni](ClO₄)₂. To a solution of Pd(TTU) (238 mg) in chloroform (15 mL) was added a solution of nickel perchlorate (251 mg) in acetonitrile (6 mL). The reaction mixture was stirred for up to 12 h. To the mixture was added diethyl ether (20 mL) and the precipitate filtered, washed with diethyl ether, and dried in vacuo; yield quantitative. Anal. Calcd for C₁₄H₂₈Cl₂NiO₈Pd₂S₈: C, 18.2; H, 3.06. Found: C, 17.6; H, 2.92.

Bis(1,4,8,11-tetrathiaundecanato)zinc Acetate, [Zn₂(TTU)₂(OAc)₂. To a stirred suspension of zinc acetate in acetone solvent was added excess TTU. A white precipitate immediately formed. The precipitate was sequentially washed with water, ethanol, and then diethyl ether and dried in vacuo. Anal. Calcd for C₁₈H₃₄O₄S₄Zn: C, 28.2; H, 4.47. Found: C, 28.6; H, 4.56. IR spectrum shows ν(CH₃CO₂⁻) at 1540 cm⁻¹.

[Bis(1,4,8,11-tetrathiaundecanato)trinickel] Tetracyanoquinodimethane, [Ni₃(TTU)₂](TCNQ)₂. The complex was prepared as an insoluble dark precipitate by mixing acetonitrile solutions of [Ni₃(TTU)₂](BF₄)₂ and Li⁺ TCNQ⁻ in a mole ratio of 1:2. The product was washed with acetonitrile and then diethyl ether and dried in vacuo. Anal. Calcd for C₃₈H₃₆Ni₃N₄S₈: C, 44.0; H, 3.49; N, 10.8; S, 24.7. Found: C, 43.9; H, 3.76; N, 10.6; S, 24.2.

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Registry No. Pt(2-PrS)₂(PPh₃)₂, 72137-83-8; Pt(2-PrS)₂(AsPh₃)₂, 72137-84-9; [[Pt(2-PrS)₂(PPh₃)₂]₂Ni](ClO₄)₂, 72137-86-1; [[Pt(PhS)₂(PPh₃)₂]₂Ni](ClO₄)₂, 72137-88-3; [[Pd(PhS)₂dppe]₂Ni](ClO₄)₂, 72137-90-7; [[Ni(PhS)₂dppe]₂Ni](ClO₄)₂, 72137-92-9; Pd(TTU), 72137-93-0; [[Pd(TTU)₂Ni](ClO₄)₂, 72137-95-2; [Zn₂(TTU)₂](OAc)₂, 72137-97-4; [Ni₃(TTU)₂](TCNQ)₂, 72173-17-2; [Ni₃(TTU)₂](BF₄)₂, 59738-24-8; Pt(PhS)₂(PPh₃)₂, 72173-18-3; [Pt(PhS)₂]_n, 59738-65-7; Pt(PhS)₂(PMe₂Ph)₂, 72173-19-4; Pt(PhS)₂(diars), 59765-76-3; Pt(SCH₂CH₂S)(PPh₃)₂, 56213-51-5; Pt(PhS)₂(AsPh₃)₂, 72137-98-5; [Pd(PhS)₂]_n, 59738-64-6; Pd(PhS)₂(PMe₂Ph)₂, 59738-10-2; Pd(PhS)₂(diars), 59738-11-3; Pd(PhS)₂(dppe), 33971-07-2; [Pd(SCH₂CH₂S)(PPh₃)₂, 56213-52-6; Ni(SCH₂CH₂S)dppe, 56213-47-9; Ni(PhS)₂dppe, 62637-81-4; Pd(SCH₂CH₂S)dppe, 72138-04-6; [Ni₃(SCH₂CH₂NH₂)₄Cl₂, 29993-19-9; [Ni₃(SCH₂CH₂NH₂)₄](TCNQ)₂, 72173-20-7; [Ni₃(SCH₂CH₂NH₂)₄]-[Ni(S₂C₂(CN)₂)₂], 72173-21-8; [Ni₃(TTU)₂][Ni(S₂C₂(CN)₂)₂], 72173-22-9; [Ni₃(TTU)₂][Co(S₂C₂(CN)₂)₂], 72173-23-0; [Ni₃(TTU)₂][Fe(S₂C₂(CN)₂)₂], 72173-24-1; *cis*-PtCl₂(PPh₃)₂, 15604-36-1.

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Binuclear Metal Carbonyls: Molecular Structure of μ -Chloro- μ -(diphenylphosphido)-hexacarbonyldiiron (Fe-Fe)

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We recently described a synthetic route to the halo-bridged binuclear iron carbonyls Fe₂(CO)₆(X)(PPh₂) (X = Cl, Br, I).¹ These compounds are potentially useful reagents for generating coordinatively unsaturated binuclear iron fragments via treatment with soluble silver salts and precipitation of silver halide. The chloro complex Fe₂(CO)₆(Cl)(PPh₂) is the first chloro-bridged iron carbonyl to be described, and we report herein details of the crystal and molecular structure.

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