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Syntheses and Characterization of Nickel Group Complexes of Two New 1,2-Dithiolenes Containing the Tetrathioethylene Unit*

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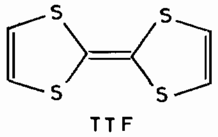
Abstract

The synthesis of the 1,2-dithiolene dianion, (bis(methylthio)-1,2-dithiolate: MTDT^{2-}) along with bis complexes with Ni(III), Pd(III) and Pt(III) are reported. In addition, the syntheses of the Pt(III) and Pd(III) complexes of a second 1,2-dithiolene (5,6-dihydro-1,4-dithiin-2,3-dithiolate: DDDT^{2-}) which also contains the tetrathioethylene unit are reported. The reduced, M(II), complexes can also be isolated in an air free environment. Cyclic voltammetric data for each complex were typical of 'dithiolenes'. These data allowed the authors to determine a stability order for 1,2-dithiolene complexes for both M(II) and M(III) oxidation states. ESR data were obtained for all new M(III) complexes. A rhombic symmetry was evident from the presence of three well defined *g* values in frozen glass spectra. We were able to utilize the Maki approach to determine the ground state electronic configurations for the Ni(III) and Pd(III) complexes. Those results support a d_{yz} HOMO for both Ni(III)L$_2^{2-}$ and Pd(III)L$_2^-$. Comparison of the Pt(III) data with that for other Pt(III) dithiolenes suggest a $^2B_{2g}$ ground state.

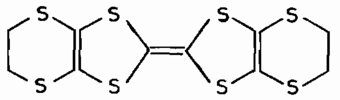
Introduction

Over the past ten years the organic chemistry of sulfur has been highly influenced by the unique physical properties of tetrathiafulvalene (TTF) [1–4]. The early proposal by Wudl [5] and others that the TTF framework might yield the prerequisite properties necessary to yield an 'organic metal' coupled with the recent findings that tetramethyltetraselenofulvalene perchlorate was a conductor at 1 K [6] have further increased the interest in this area. At the same time, there has been a great deal of interest in inorganic complex based conducting species. Examples such as the partially oxidized tetracyanoplatinates have prompted many laboratories to explore new complexes in this area [7]. A scheme to combine the properties of the 'TTF type' organosulfur molecules and the inorganic systems which have been recently studied has been designed. Since it is apparently the tetrathioethylene unit of TTF which is fundamentally important to that class of molecule, we have undertaken a synthetic program to investigate inorganic complexes of new ligands containing this sub-unit.

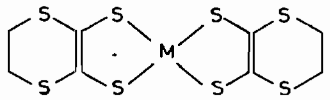


TTF

We recently reported the synthesis of the dianion 5,6-dihydro-1,3-dithiin-2,3-dithiolate (DDDT)$^{2-}$ and detailed studies of the nickel [8] and copper [9] complexes of this 1,2-dithiolene. It was found that the 'Ni(III) and Cu(III)' complexes of DDDT were similar in many respects to other monoanionic nickel and copper dithiolenes. It was also noted that a number of similarities exist between these M(DDDT)$_2^-$ systems (M = Ni, Cu) and the BEDT–TTF in (BEDT–TTF)$_2$ReO$_4$ [10] particularly in the nickel(III) case.



BEDT-TTF



M(DDDT)$_2^-$

These similarities and the fact that (BEDT–TTF)$_2$-ReO$_4$ [11] was the first totally sulfur based superconductor have prompted our further investigation into the coordination chemistry of (DDDT)$^{2-}$. Quite recently, Schultz *et al.* [12] reported the synthesis and crystal structure of Au(DDDT)$_2$ and the synthesis and crystal structure of an additional salt of the Ni(DDDT)$_2^-$ anion, a structure in which stacking occurs among the anions.

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We report here the synthesis of the Pt(III) and Pd(III) complexes of $(DDDT)^{2-}$ and their physical properties. We also report the synthesis of another new 1,2-dithiolene ligand which like $(DDDT)^{2-}$ contains the tetrathioethylene unit, dipotassium 1,2-bis(methylthio)-1,2-dithiolate (MTDT). We have synthesized and characterized the Ni(III), Pt(III) and Pd(III) complexes of this ligand.

Experimental

Reagents

2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-on (TTBEO) and 4,5-bis(methylthio)-1,3-dithiol-2-on (MTDO) were prepared by literature methods and characterized by NMR and melting points (m.p.) [13]. Bis(benzonitrile)palladium(II)chloride, tetraethylammonium bromide, potassium tetrachloroplatinate, and platinum(II)chloride were obtained from Aldrich Chemicals. The tetraethylammonium bromide was recrystallized from ethanol and dried *in vacuo* at 140 °C prior to use. Tetrabutylammonium perchlorate was purchased from Fisher Scientific and was used without further purification. Nickel chloride hexahydrate was purchased from Matheson, Coleman, and Bell, Inc. Ar was purchased from Air Products, Inc. All solvents were dried by standard techniques, freshly distilled prior to use, and degassed by successive freeze–thaw cycles when necessary. K_2DDDT was prepared as described earlier [8].

Procedures

All reactions were carried out under Ar using standard Schlenk techniques unless otherwise stated. Analyses were performed by Atlantic Microlabs, Atlanta, Ga.

Syntheses

$K_2(C_4H_6S_4)$

MTDO (5 g, 2.4×10^{-2} mol) was added to 200 ml of dry THF containing 9.6×10^{-2} mol of potassium ethoxide. A yellow–orange precipitate formed immediately; the mixture was allowed to stir overnight after which 100 ml of chilled hexanes were added. The precipitate was then collected, dried, and stored in a Schlenk tube until further use. Because of extreme air sensitivity, an elemental analysis of MTDT was not obtained. Yield 90%; ^1H NMR (d_6-DMSO): $\delta = 2.5$ (s), CH_3–S. The dianion is extremely air sensitive as a solid, however, it is relatively stable for short periods of time in solution exposed to air, and further reactions were carried out without the use of an Ar atmosphere.

$N(C_2H_5)_4Ni(C_4H_6S_4)_2$

A solution of 0.46 g (1.9×10^{-3} mol) of $NiCl_2 \cdot 6H_2O$ in 10 ml of H_2O was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2MTDT in 50 ml of 50/50 (v/v) ethanol/water. The solution immediately turned brown and was allowed to stir for 1 h after which 1 equivalent of tetraethylammonium bromide in 25 ml of ethanol was added and a brown precipitate formed. This brown solid was then collected by filtering and recrystallized from acetonitrile, yielding 0.5 g (50%) of pure product as brown crystalline plates (m.p. 200 °C dec.). *Anal.* Calc. for $NiC_{16}H_{32}NS_8$: C, 34.71; H, 5.83; N, 2.53; S, 46.33. Found: C, 34.52; H, 5.73; N, 2.46; S, 46.17%. IR (KBr) 2980(s), 2905(m), 1482(s), 1430(m), 1350(s), 1310(s), 1171(s), 1065(m), 1000(m), 965(m), 875(m), 780(m), 44(m), 379(m).

$N(C_2H_5)_4Pd(C_4H_6S_4)_2$

A solution of 0.75 g (1.92×10^{-3} mol) of bis(benzonitrile)palladium(II) chloride in 50 ml of THF was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2MTDT in 100 ml of THF. The solution slowly turned red–brown as the ligand reacted and it was allowed to stir for 1 h after which 1 equivalent of tetraethylammonium bromide in 25 ml of H_2O was added. The volume of the solution was reduced by half and a red–brown solid formed which was collected by filtering, washed with ether, dried, and recrystallized from acetonitrile yielding 0.6 g (50%) of pure product as a red–brown microcrystalline solid (m.p. 200 °C dec.). *Anal.* Calc. for $PdC_{16}H_{32}NS_8$: C, 32.07; H, 5.04; N, 2.34; S, 42.80. Found: C, 32.15; H, 5.09; N, 2.40; S, 42.71%. IR (KBr) 2985(m), 2910(s), 1479(m), 1425(s), 1300(m), 1180(m), 1170(m), 1125(m), 1000(w), 960(m), 850(s), 780(m), 545(w), 438(w).

$N(C_2H_5)_4Pt(C_4H_6S_4)_2$

A slurry of 0.50 g (1.9×10^{-3} mol) of platinum dichloride in 20 ml of water was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2MTDT in 50 ml of 1/2 (v/v) water/ethanol. The mixture was stirred for 1 h and it slowly became homogeneous as the product formed. One equivalent of tetraethylammonium bromide was then added to precipitate the product as a red–brown solid. This solid was collected by filtering, washed with ethanol, dried, and recrystallized from acetonitrile. Yield 0.60 g (46%), m.p. 120 °C. *Anal.* Calc. for $PtC_{16}H_{32}NS_8$: C, 27.85; H, 4.67; N, 2.03; S, 37.17. Found: C, 28.07; H, 4.90; N, 2.14; S, 37.50%. IR (KBr) 2980(m), 2905(m), 1455(m), 1305(m), 1175(m), 1120(m), 995(w), 965(m), 845(s), 780(m), 435(w), 380(w).

$N(C_2H_5)Pt(C_4H_4S_4)_2$

A solution of 0.81 g (1.9×10^{-3} mol) of potassium tetrachloroplatinate in 10 ml of water was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2-DDDT in 50 ml of 1/2 (*v*/*v*) water/ethanol. The solution turned brownish-green over a period of 1 h and it was allowed to stir for an additional hour, after which 1 equivalent of tetraethylammonium bromide in 25 ml of water was added to precipitate the product. This brownish-green solid was collected by filtering, washed with ethanol, dried, and recrystallized from acetonitrile. Yield 0.65 g (50%), m.p. 117–120 °C. *Anal.* Calc. for $PtC_{16}H_{28}NS_8$: C, 28.02; H, 4.08; N, 2.04; S, 37.40. Found: C, 27.95; H, 4.20; N, 2.01; S, 37.30%. IR (KBr) 2975(w), 2910(m), 1480(m), 1450(m), 1405(m), 1350(s), 1281(s), 1180(m), 1170(m), 1000(m), 950(w), 920(w), 840(m), 780(m), 430(m), 375(w).

$N(C_2H_5)_4Pd(C_4H_4S_4)_2$

A solution of 0.75 g (1.92×10^{-3} mol) of bis(benzonitrile)palladium(II) chloride in 50 ml of THF was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2DDDT in 100 ml of THF. As the reaction proceeded the solution slowly turned green. The solution was stirred for 1 h after which 1 equivalent of tetraethylammonium bromide in 50 ml of water was added. The solution volume was then reduced by half and a green precipitate formed which was collected by filtering, washed with ether, dried, and recrystallized from acetone/isopropanol to yield 0.6 g (50%) of pure product as a green microcrystalline solid (m.p. 170–172 °C). *Anal.* Calc. for $PdC_{16}H_{28}NS_8$: C, 32.19; H, 4.69; N, 2.34; S, 42.96. Found: C, 32.24; H, 4.75; N, 2.40; S, 42.85%. IR (KBr) 2980(m), 2905(m), 1472(s), 1410(m), 1390(m), 1295(s), 1250(s), 1175(s), 1130(s), 1035(s), 1000(s), 980(m), 915(m), 875(m), 830(s), 770(m), 420(s), 350(m).

Physical Measurements

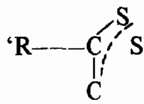
All electrochemical measurements were performed using a BAS CV27. The electrochemical cell used for cyclic voltammetry employed a platinum working electrode, a platinum wire as the auxiliary electrode, and either a SCE or a Ag/AgCl reference electrode. Measurements were made on solutions containing 10^{-3} M metal dithiolenes with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Nitrogen was passed through the solution for 15 min prior to taking the 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}. Data were obtained as KBr pellets. UV–Vis spectra were recorded on a Cary 14 spectrophotometer.

Results and Discussion

The synthesis of a new 1,2-dithiolene, dipotassium 1,2-bis(methylthio)-1,2-dithiolate (K_2MTDT) containing the tetrathioethylene unit like K_2DDDT has been achieved. This yellow salt is extremely air sensitive as a solid even though we have found it to be stable for short periods of time in solution exposed to air. The formally nickel(III), platinum(III) and palladium(III) complexes of this ligand have been synthesized and isolated as the tetraethylammonium salts. If care is taken to exclude O_2 from the reaction flask the nickel(II), platinum(II) and palladium(II) complexes can be prepared. All of these compounds are, however, rapidly oxidized by exposure to O_2.

The syntheses of the formally platinum(III) and palladium(III) complexes of $(DDDT)^{2-}$ have also been achieved. As was the case with these complexes of $(MTDT)^{2-}$ the reduced species can be easily prepared if O_2 is excluded from the reactions. These compounds are also rapidly oxidized upon exposure to O_2.

In the case of both $MTDT^{2-}$ and $DDDT^{2-}$ different synthetic procedures were required to prepare the platinum and palladium complexes. The procedure used to prepare the platinum complex of both ligands was very similar to that used to prepare the nickel complexes of these ligands. Aqueous solutions of the metal were added to water/alcohol solutions of the ligand and the products were formed in a standard metathesis format and tetraethylammonium bromide was used as the counter-ion to precipitate the product. When this type of reaction scheme was tried for palladium (using aqueous solutions of $PdCl_2$ or K_2PdCl_4) only insoluble metal sulfides were obtained. We were able to prepare the palladium complex using THF as a solvent system and bis(benzonitrile)palladium(II)chloride as our palladium source. Since the ligand was only slightly soluble in THF and the product was soluble the rapid formation of metal sulfides could be avoided. The work-up procedure was not quite as easy even though pure product was obtained in respectable yield.

All of the Ni, Pd, and Pt complexes of both $(DDDT)^{2-}$ and $(MTDT)^{2-}$ display very rich IR spectra with all the characteristic absorptions of monoanionic metal dithiolenes present [14]: ν_1, ‘C═══C’ around 1450 cm^{-1}; ν_2, ‘C═══S’ around 1170 cm^{-1}; ν_3,  around 850 cm^{-1}; and ν_4 and ν_5, ‘M–S’ around 400 and 500 cm^{-1}, respectively. The IR spectral data for the Ni, Pd, and Pt complexes of $(DDDT)^{2-}$ and $(MTDT)^{2-}$ are summarized in Table I.

With the exception of the nickel complex of $(MTDT)^{2-}$, cyclic voltammograms of all of the metal complexes of $(DDDT)^{2-}$ and $(MTDT)^{2-}$ reported here revealed two well defined reversible waves.

TABLE I. IR data (cm^{-1}, for Ni, Pd and Pt Complexes of (DDDT)$^{2-}$ and (MTDT)$^{2-}$

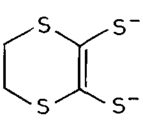
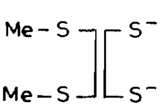
		Ni(III)	Ni(II)	Pd(III)	Pt(III)
	ν_1	1415	1410	1425	1450
	ν_2	1170	1165	1180	1170
	ν_3	855	855	850	841
	ν_4	475	441	545	430
	ν_5	410	385	438	375
		Ni(III)	Pd(III)	Pt(III)	
	ν_1	1479	1472	1455	
	ν_2	1170	1175	1175	
	ν_3	870	875	845	
	ν_4	445	420	435	
	ν_5	380	350	380	

TABLE II. Voltammetric Data of Group VIII Metal Dithiolenes Couple: $[ML_2]^{1-} + e^- \rightleftharpoons [ML_2]^{2-}$ (volts)

M	Ligand	$E_{1/2}$ (DMF *vs.* Ag/AgCl)
Ni	DDDT^{2-}	−0.81
	MTDT^{2-}	−0.67
	dmit^{2-}	−0.19^a
	MNT^{2-}	+0.259^b
Pd	DDDT^{2-}	−0.43
	MTDT^{2-}	−0.45
	dmit	−0.09^a
	MNT^{2-}	+0.473^b
Pt	DDDT^{2-}	−0.59
	MTDT^{2-}	−0.59
	dmit	−0.27^a
	MNT^{2-}	+0.243^b

^{a}CH$_3$CN *vs.* SCE (ref. 15). ^{b}Ref. 16.

TABLE III. Voltammetric Data of Group VIII Metal Dithiolenes Couple: $[ML_2]^0 + e^- \rightleftharpoons [ML_2]^-$ (volts)

M	Ligand	$E_{1/2}$ (DMF *vs.* Ag/AgCl)
Ni	DDDT^{2-}	+0.014
	MTDT^{2-}	+0.10^a
	MNT^{2-}	+1.049^b
Pd	DDDT^{2-}	+0.21
	MTDT^{2-}	+0.18
	MNT^{2-}	+0.996^b
Pt	DDDT^{2-}	+0.02
	MTDT^{2-}	+0.19
	MNT^{2-}	+0.853^b

^{a}(E_p) irreversible wave with scan rates of 50–500 mV/s. ^{b}Ref. 16.

These data are summarized in Tables II and III along with the results of studies on some other group VIII metal dithiolene complexes.

A careful examination of the voltammetric data reveals some interesting trends. For nickel group complexes of MNT^{2-} and dmit^{2-}, we find a stability order of Pd > Ni > Pt for the dianionic species. In the DDDT^{2-} and MTDT^{2-} cases we find a stability order to make a direct comparison of the relative prder to make a direct comparison of the relative stabilities of the neutral, monoanionic and dianionic forms of all four of these ligands we can compare the voltammetric data of the nickel complex of each. We find a dianionic stability order of MNT^{2-} > dmit^{2-} > MTDT^{2-} > DDDT^{2-}. It has been previously shown that trends of this type follow the electron withdrawing ability of the dithiolene ligand [17], *i.e.* the greater the electron attracting ability of the ligand the more easily the complex can accommodate the larger number of valence electrons. This does not, however, appear to be the case when comparing MTDT^{2-} and DDDT^{2-}, since one would expect the CH$_3$–S groups in MTDT^{2-} to be less electron withdrawing than the –CH$_2$–CH$_2$–S group of DDDT^{2-}. This leads to the conclusion that DDDT^{2-} should be more stable as the dianion than MTDT^{2-} which is opposite to the experimental result. This problem can be resolved by comparing the HOMO of each complex. The only difference in the two ligands is that in MTDT^{2-} there is free rotation about the C–S–Me bond whereas in DDDT^{2-} this is not possible. This rotation disrupts some of the anti-bonding character of the HOMO in MTDT^{2-} and hence lowers its energy, making it easier to be reduced.

As is the case with other monoanionic nickel dithiolenes both Ni(DDDT)$_2^-$ and Ni(MTDT)$_2^-$ show intense absorptions in the low energy visible and near infrared regions. A comparison of the optical data of the monoanionic nickel complexes of DDDT^{2-} and MTDT^{2-} is shown in Table IV with suggested assignments based on earlier work by Schrauzer and Mayweg [18].

The frozen glass ESR spectrum of Ni(MTDT)$_2^-$ like that of Ni(DDDT)$_2^-$ shows a rhombic g tensor with slightly smaller g values. The solution ESR spectra of both Pd(MTDT)$_2^-$ and Pd(DDDT)$_2^-$ clearly show four of the six lines expected for the interaction of an unpaired electron with a palladium-105 nucleus ($I = 5/2$, 22% natural abundance). The two central lines are hidden beneath the more intense $I = 0$ line. The frozen glass spectra of the Pd complexes of both MTDT^{2-} and DDDT^{2-} revealed a rhombic g tensor with only slight deviations from axial symmetry ($g_y - g_x = 0.004$ and 0.007). The interpretation of the frozen glass spectrum of Pd(DDDT)$_2^-$ was straightforward, however, this was not true for the frozen glass spectrum of

TABLE IV. Electronic Spectra of $Ni(DDDT)_2^-$ and $Ni(MTDT)_2^-$

	Maxima (ϵ) (cm^{-1})	Suggested assignment
$Ni(DDDT)_2^-$ (DMF)	7955(4490)	$\pi \rightarrow \pi$
	9009(4910)	$\pi \rightarrow \pi$
	16447(932)	$\pi \rightarrow M$
	25640(2895)	$M \rightarrow \pi$
$Ni(MTDT)_2^-$ (DMF)	9346(7620)	$\pi \rightarrow \pi$
	15625(909)	$\pi \rightarrow M$
	17857(1091)	$n_{=s} \rightarrow M$
	25906(2600)	$\pi \rightarrow M$
	31747(22727)	$\pi \rightarrow \pi$

$Pd(MTDT)_2^-$ since we were unable to obtain a quality glass spectrum in this latter case.

The solution ESR spectra of both $Pt(MTDT)_2^-$ and $Pt(DDDT)_2^-$ show the two lines expected for the interaction of the unpaired electron with single platinum-195 nucleus ($I = 1/2$, 33.8% natural abundance) and also the strong central $I = 0$ line. The frozen glass spectra of both $Pt(MTDT)_2^-$ and $Pt(DDDT)_2^-$ show a rhombic g tensor with greater deviations from axial symmetry than either the Ni or Pd complexes. The interpretations of both frozen spectra were straightforward.

The ESR results for the Ni, Pd and Pt complexes of $DDDT^{2-}$ and $MTDT^{2-}$ as well as $dmit^{2-}$ and mnt^{2-} are given in Table V. In our previous work we showed that $Ni(DDDT)_2^-$ has the same $^2B_{2g}$ ground state as $Ni(mnt)_2^-$ and $Ni(dmit)_2^-$, which is composed of metal d_{xy} and out of plane sulfur $2p_z$ orbitals. In this case we have examined the Pd and Pt complexes of $DDDT^{2-}$ and $MTDT^{2-}$ to determine if they have the same $^2B_{2g}$ ground state as those of $dmit^{2-}$ and mnt^{2-}. We accomplished this using the equations of Maki *et al.* [19] as before [8] for a d_{yz} ground state which relate g and A values to the bonding parameters P and K through configurational excitation energies C_i. Using this treatment for various ground state possibilities, we found the $d_{yz}{}^1d_{xy}$ most reasonable for the Pd complexes of $DDDT^{2-}$, $MTDT^{2-}$, and $dmit^{2-}$. This is in agreement with the results Maki obtained for $Pd(mnt)_2^-$ [19]. Using the reduction of P from its free ion value (27.5×10^{-4} cm^{-1}) as a measure of covalency, we calculated the ratio P/P_0, a measure of the metal spin density. A summary is shown in Table V. The P/P_0 values for all four of these palladium complexes are between 0.19 and 0.24 indicating a highly delocalized ground state orbital in each case.

Unfortunately since no P_0 value is available for platinum(III) we were unable to use this procedure to evaluate the ground states for the platinum complexes. Kirmse *et al.*, however, have shown by examination of the ^{33}S superhyperfine splittings in $Pt(mnt)_2^-$ that it has a $^2B_{2g}$ ground state orbital which is extensively delocalized over the ligands [21]. Based on the similarity of the ESR parameters of $Pt(DDDT)_2^-$, $Pt(MTDT)_2^-$, and $Pt(dmit)_2^-$ we feel it is reasonable to conclude that these complexes also have a highly delocalized $^2B_{2g}$ ground state.

Conclusions

K_2DDDT and K_2MTDT are two of only three ligands to date which contain the tetrathioethylene unit, the other being K_2dmit. We have shown previously that $Ni(DDDT)_2^-$ and $Ni(dmit)_2^-$ had many similar structural and electronic properties. In this work we have again found similarities in the Pt and Pd complexes of these two ligands as well as with those of $MTDT^{2-}$. As shown by comparing the spin Hamiltonian parameters of all of the compounds

TABLE V. ESR Results for Ni, Pd and Pt Dithiolenes[a]

Compound	g_{iso}[b]	g_{xx}	g_{yy}	g_{zz}	A_{iso}[c]	A_{xx}	A_{yy}	A_{zz}	P/P_0	K	Reference
$Ni(DDDT)_2^-$	2.057	2.119	2.057	2.022	−4.5	−14.2	2.4	<0.2	0.21	0.25	8
$Ni(MTDT)_2^-$	2.051	2.093	2.051	2.014							this work
$Ni(dmit)_2^-$	2.049	2.105	2.041	2.001	4.07	13	−5.3	4.5	0.22	0.13	21
$Ni(mnt)_2^-$	2.063	2.160	2.042	1.988	−4.6	−15	2.9	<2	0.24	0.21	19, 20
$Pd(DDDT)_2^-$	2.038	2.056	2.063	1.992	6.3	9.0	6.7	4.1	0.24	0.92	this work
$Pd(MTDT)_2^-$	2.038	2.053	2.057	1.989	6.4	9.5	5.4	5.0	0.22	1.132	this work
$Pd(dmit)_2^-$	2.019	2.044	2.045	1.967	6.7	5.4	10.0	4.8	0.25	1.00	21
$Pd(mnt)_2^-$	2.024	2.070	2.044	1.956	8.2	9.0	6.3	5.5	0.19	1.33	19, 20
$Pt(DDDT)_2^-$	2.059	2.174	2.084	1.900	82.7	29.5	98.4	89.2			this work
$Pt(MTDT)_2^-$	2.057	2.179	2.086	1.903	81.6	30.5	99.9	74.6			this work
$Pt(dmit)_2^-$	2.033	2.073	2.168	1.858	−67.0	−99.2	−21.8	−78.1			21
$Pt(mnt)_2^-$	2.042	2.065	2.245	1.827	78.0	−125.5	0.0	−99.1			21

[a] Solution spectra for compounds studied in this work were obtained in DMF, frozen glasses in 50/50 DNF/CH_2Cl_2. [b] Standard deviations of g values is 0.001. [c] A value in units of $cm^{-1} \times 10^{-4}$.

of $DDDT^{2-}$, $MTDT^{2-}$ and $dmit^{2-}$ we see that both the platinum and palladium complexes of all three ligands have the same type of highly delocalized π MO as the HOMO. As was the case of the nickel complexes of $DDDT^{2-}$ and $dmit^{2-}$ the platinum and palladium complexes show some differences in their redox behavior. All of the complexes of $dmit^{2-}$ are more easily reduced to the dianions than are those of either $DDDT^{2-}$ or $MTDT^{2-}$. The greater electron accepting ability of the thioketone function in $dmit^{2-}$ as compared to the ethylene unit and methyl groups in $DDDT^{2-}$ and $MTDT^{2-}$, respectively, is largely responsible for this difference.

As we have mentioned in the past, the discovery of superconductivity in $(BEDT{-}TTF)_2ReO_4$ has been a driving force in our continued interest in metal complexes of $DDDT^{2-}$ and $MTDT^{2-}$. This work is a continuation of our efforts to locate new highly conducting materials.

Supplementary Material

Cyclic voltammograms and ESR spectra for all complexes (14 figures) are available from the authors on request.

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