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Semiconducting Metal–Organic Salts

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Electron-transfer salts including metal complex ions of the "metal dithiolene" type form semiconducting solids with specific (compaction) resistivities of 10^2–10^8 ohm-cm. Salts in which both ions were metal complexes, as well as those in which one ion was organic and one was a metal complex were obtained from metathesis reactions generally as dark microcrystalline powders. The best conductors found included bis(*o*-phenylenediimine)nickel bis(ethenedithiolato)nickelate ($\rho_{300} \approx 600$ ohm-cm), bis(*o*-phenylenediimine)nickel bis(toluenedithiolato)nickelate (400 ohm-cm), bis(4,5-dimethyl-1,2-phenylenediimine)nickel bis(maleonitriledithiolato)nickelate (2600 ohm-cm), bis(*o*-phenylenediimine)palladium bis(ethenedithiolato)nickelate (2000 ohm-cm), tetrathiafulvalene bis(maleonitriledithiolato)nickelate (600 ohm-cm), *N*-methylphenazinium bis(ethenedithiolato)nickelate (2000 ohm-cm), and phenoxazine bis(hexafluoro-2-butene-2,3-dithiolato)nickelate (3600 ohm-cm). No single-crystalline samples of any interesting compounds could be obtained, principally because of decomposition reactions which take place in those solvents (DMF, DMSO) in which the salts are soluble. Procedures for the preparation of hexafluoroantimonate salts of the bis(*o*-phenylenediimine)nickel, tetrathiafulvalene, and thianthrene cations are presented.

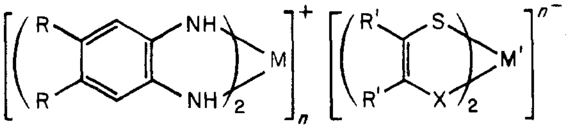
The recent reports of high electrical conductivity in salts of tetracyanoquinodimethane (TCNQ), particularly with the radical cation of tetrathiafulvalene (TTF),[1] and platinum and iridium complexes,[2] have generated renewed interest in the electrical properties of organic and metalloorganic materials. Our interests were directed toward the square-planar transition metal–dithiolene type complexes.[3] These complexes exhibit a rich redox chemistry; furthermore, crystal structures of several of their salts show stacking arrangements suggestive of intermolecular electronic interaction in the solid state similar to that found in the TCNQ[4] and Krogman-type platinum complex salts.[2]

Surprisingly few reports have appeared of work in the electrical properties of these complexes. Schrauzer[5] has reported the resistivities of compactions of several neutral complexes. The perylene and pyrene charge-transfer complexes of $Ni(thiete)_2$ reported by Schmitt et al.[6] are two of the most highly conducting heterosoric compounds[7] yet reported. More recently, conducting complexes of metal dithiolenes with various organic donors have been described.[9]

In this paper we report the preparation and electrical properties of salts formed from bis(*o*-phenylenediimine)metal and related cations with several bis(1,2-dithiolato)metal anions and the salts of both of these ions with various planar organic ions.

Results and Discussions

Transition Metal–Dithiolene and Related Complex Ion Salts. The complex metal salts studied (Table I) have in common the formulation



where M = Ni, Pd; R = H, CH_3; M' = Ni, Pd, Pt, Co, Cu, Fe; X = NH, S; R' = H, CN; R', R' = C_4H_4. They were prepared by metathesis from suitable salts of the component metal complex ions which were generally synthesized by established methods.[3] (The preparation of several new complex ions is described in the Experimental Section together with improved procedures for a few of the previously reported ions.)

Table I. Semiconducting Metal–Organic Salts

No.	Salt[a]	log ρ_{300}	S_{310}, μV deg^{-1}
1	$\mathrm{Ni(opd)_2{}^+SbF_6{}^-}$	9.78	
2	$\mathrm{Pd(opd)_2{}^+SbF_6{}^-}$	8.60	
3	$\mathrm{Ni(dmopd)_2{}^+SbF_6{}^-}$		
4	$\mathrm{Ph_3PMe^+Ni(mnt)_2{}^-}$	10.70	
5	$\mathrm{Ni(opd)_2{}^+Ni(edt)_2{}^-}$	2.76[b,f]	−180
6	$\mathrm{Pd(opd)_2{}^+Ni(edt)_2{}^-}$	3.30	−320
7	$\mathrm{Pd(opd)_2{}^+Pd(edt)_2{}^-}$	4.63	−50
8	$\mathrm{Ni(dmopd)_2{}^+Ni(edt)_2{}^-}$	6.21	
9	$\mathrm{Ni(dmopd)_2{}^+Ni(ibt)_2{}^-}$	5.52	
10	$\mathrm{Ni(opd)_2{}^+Ni(bdt)_2{}^-}$	3.40	0[e]
11	$\mathrm{Ni(opd)_2{}^+Ni(tdt)_2{}^-}$	2.60[c,f]	0[e]
12	$\mathrm{Ni(dmopd)_2{}^+Ni(tdt)_2{}^-}$	8.15	
13	$\mathrm{[Ni(opd)_2{}^+]_2[Co(tdt)_2]_2{}^{2-}}$	3.86	−110
14	$\mathrm{[Ni(dmopd)_2{}^+]_2[Co(tdt)_2]_2{}^{2-}}$	9.06	
15	$\mathrm{[Ni(opd)_2{}^+]_2[Fe(tdt)_2]_2{}^{2-}}$	4.45	
16	$\mathrm{[Ni(dmopd)_2{}^+]_2[Fe(tdt)_2]_2{}^{2-}}$	8.41	
17	$\mathrm{Ni(dmopd)_2{}^+Ni(mnt)_2{}^-}$	3.42[d,f]	+355
18	$\mathrm{Ni(opd)_2{}^+Ni(mnt)_2{}^-}$	5.92	+40
19	$\mathrm{[Ni(opd)_2{}^+]_2Ni(mnt)_2{}^{2-}}$	5.10	−700
20	$\mathrm{[Ni(dmopd)_2{}^+]_2Ni(mnt)_2{}^{2-}}$	>7	

[a] Abbreviations: opd, *o*-phenylenediimine; dmopd, 4,5-dimethyl-*o*-phenylenediimine; mnt, maleonitriledithiolato; edt, ethylenedithiolato; ibt, 2-iminobenzenethiolato; bdt, 1,2-benzenedithiolato; tdt, toluenedithiolato. [b] $E_a = 0.24$ eV. [c] $E_a = 0.17$ eV. [d] $E_a = 0.33$ eV. [e] These materials showed a marked dependence on temperature, with S changing sign at ambient temperature. [f] Four-probe measurement.

In the course of the work it was observed that neutral bis(*o*-phenylenediimine)nickel [$Ni(opd)_2$] was polymorphic, one crystalline form appearing to be dark green and the other gold. Either form can be induced by appropriate seeding of crystallization solutions. The "dark green" form, from X-ray powder pattern measurements, appears to be identical with that on which Hall and Soderberg[10] performed a single-crystal structure determination. The "gold" form has a different structure,[11] apparently not identical with that of Hall and Soderberg's "lost" crystal.

The salts, **5–20** (Table I), precipitate from reaction solutions as dark, microcrystalline or amorphous powders which are insoluble in water and all the common organic solvents, although slightly soluble (with decomposition) in dimethylformamide and dimethyl sulfoxide. Consequently, attempts to purify these salts further or grow crystals for structural studies and electrical measurements by simple solution techniques failed; more elaborate techniques were not attempted.

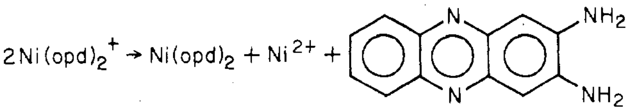
Two modes of decomposition have been observed. The first, ligand exchange, occurs when salts of the $Ni(opd)_2{}^+Ni(mnt)_2{}^-$ type dissolve in donor solvents, yielding "mixed", neutral

Table II.

No.	Salt[a]	log ρ_{300}	S_{310}, μV deg^{-1}
21	$CV^+Ni(mnt)_2^-$	8.5	
22	$An_3C^+Ni(mnt)_2^-$	8.5	
23	$MG^+Ni(mnt)_2^-$	8.5	
24	$NMP^+Ni(mnt)_2^-$	7.7	
25	$Thian^+Ni(mnt)_2^-$	4.48	
26	$WB^+Ni(mnt)_2^-$	5.67[d]	−500
27	$NMP^+Ni(edt)_2^-$	3.30	−50
28	$NMP^+Ni(tdt)_2^-$	>7	
29	$Phthi^+Ni(thiete)_2^-$	>8[d]	
30	$Phox^+Ni(thiete)_2^-$	3.56[d]	−80
31	$TTF^+Ni(mnt)_2^-$	2.80[b,d]	−655
32	$TTF^+Cu(mnt)_2^-$	4.63	−500
33	$(TTF^+)_2[Co(mnt)_2]_2^{2-}$	3.39[c]	−427
34	$(TTF^+)_2[Fe(mnt)_2]_2^{2-}$	3.70	−470
35	$TTF^+Pd(mnt)_2^-$	3.67	−230
36	$TTF^+Pt(mnt)_2^-$	3.86	−410
37	$(TTF^+)_2Ni(mnt)_2^{2-}$	4.88	+30
38	$(TTF^+)_2Cu(mnt)_2^{2-}$	6.30	
39	$TCNTTF^+Ni(mnt)_2^-$	7.48	
40	$TTT^+Ni(mnt)_2^-$	2.51	−170
41	$Ni(dmopd)_2^+TCNQ^-$	4.87	+300
42	$[Ni(opd)_2]_2^+TCNQ^-$	4.54	+10
43	$[Pd(opd)_2]_2^+TCNQ^-$	4.95	+420

[a] Abbreviations: CV, crystal violet; An_3C, tris(*p*-methoxyphenyl)carbene; MG, Malachite Green; NMP, *N*-methylphenazine; Thian, thianthrene; WB, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Wurster's Blue); Phthi, phenothiazine; Phox, phenoxazine; TCNTTF, 4,4',5,5'-tetracyano-$\Delta^{2,2'}$-bi-1,3-dithiole (tetracyanotetrathiafulvalene); TTT, tetrathiotetracene. [b] E_a = 0.15 eV. [c] E_a = 0.24 eV. [d] Four-probe measurement.

complexes, e.g., Ni(opd)(mnt), similar to those recently reported by Miller and Dance.[12] The second is disproportionation of *o*-phenylenediimine ligands and appears to go as



The organic product, 2,3-diaminophenazine, is a common product of the oxidation of *o*-phenylenediamine in the presence of transition metal ions.[13] The 4,5-dimethyl-1,2-phenylenediimine ligand apparently gives 4,8-diamino-1,2,5,6-tetramethylphenazine on disproportionation. Under conditions where both reactions might occur, only ligand exchange is observed, suggesting that it is the faster of the two.

The electrical resistivity (ρ) and thermoelectric power (S) of these salts are given in Table I.

The temperature dependence of three of these materials, **5**, **11**, and **17**, has been measured, and activated behavior, typical of semiconductors, was observed. These lead us to suggest that the majority of the new materials with compaction, room-temperature resistivities, ρ, in the 10^3–10^6 ohm-cm range are semiconductors.

Metal–dithiolene complexes are generally found to have their anions associated in pairs or columns in the crystal lattice.[3,14] Structural arrangements of this type in TCNQ compounds,[6] etc., generally promote conductivity and, by analogy, these complexes probably have a similarly broad variation in crystal structure[4,8] and mode of electronic interaction.

Salts of Organic Molecular Ions with Transition Metal–Dithiolene and Related Complex Ions. These salts (**21–43**, Table II) were prepared by metathesis from solutions. Improved procedures for the preparation of certain component ions are again given in the Experimental Section. These materials were generally obtained as well-defined, crystalline compounds and could usually be purified by normal recrystallization procedures. However, attempts to recrystallize *o*-phenylenediiminemetal salts (**41–43**) lead to decomposition to 2,3-diaminophenazine as discussed above.

The electrical properties of these salts are given in Table II. The electrical measurements were obtained on compacted powders. The lowest resistivities were observed with the TTF and TTT salts, the smallest being recorded for the bis(maleonitriledithiolato)nickel salts, **31** and **40**, the TTF salt having a value similar to that reported by Wudl et al.[9]

While compaction studies are useful as a general guide to the identification of materials with interesting electrical properties, discussions based on such measurements can often be quite misleading. Unfortunately, attempts to grow single crystals of the low-resistivity (TTF)Ni (mnt)$_2$ invariably failed, giving instead the higher resistivity $(TTF)_2Ni(mnt)_2$, **37**. Nonetheless, it seems likely that, in the lower resistivity salts of TTF^+ and TTT^+, the conduction paths involve aggregates of these species.

Experimental Section

Physical Measurements. Electrical measurements were obtained by conventional two- and four-electrode techniques on compactions pressed at 90,000 psi in a micropellet press of dimensions 1 mm × 5 mm. Silver/PVC paint (Micro-Circuits Corp. SC-15 or Du Pont Co. No. 4929) was used to make electrical contact between the probes and the pellet. Such contacts were found to be ohmic by conventional tests which included current reversal and variation. Two-probe measurements were made both along the length of typically 0.5 × 1.0 × 5.0 mm compacted-powder pellets and across the short axis. Specific resistivities measured by these two operations agreed within the uncertainty of dimensional measurements, implying that contact resistances were not more than 10% of sample resistance in any case.

Preparation of Materials. Compounds **4** and **39** were prepared as described in the literature.[15,16]

Samples of **29** and **30** were kindly provided by Dr. W. E. Geiger, Southern Illinois University, Carbondale, Ill.

Analytical data are collected in Table III.

Bis(*o*-phenylenediamine)dichloronickel. Nickel chloride (glyme) (0.025 mol) Alfa Inorganics in dry deoxygenated methanol (200 ml) was treated with *o*-phenylenediamine (0.05 mol). The mixture was stirred for 0.5 hr at ambient temperature in an atmosphere of dry nitrogen. The lavender solid was collected by filtration, washed with methanol, and air-dried; yield 78%.

Bis(*o*-phenylenediimine)nickel, Ni(opd)$_2$.[17] Bis(*o*-phenylenediamine)dichloronickel (5 mmol) was suspended in purified tetrahydrofuran (75 ml) and cooled to −80° under dry nitrogen. *tert*-Butyllithium (0.06 mol) in pentane (6 ml) was added to the stirred suspension. The reaction mixture turned brown and, then, on slowly warming up to ambient temperature, became deep red. On exposure to the atmosphere a deep blue-green color developed and a solid was slowly precipitated. The product was collected by filtration, washed with water and acetone, and air-dried. The product was purified by continuous extraction into acetone; yield 45%.

Bis(*o*-phenylenediimine)nickel Hexafluoroantimonate, $Ni(opd)_2^+SbF_6^-$ (1). A suspension of $Ni(opd)_2$ (0.01 mol) in acetonitrile (100 ml) was treated with a solution of silver hexafluoroantimonate (0.01 mol) in acetonitrile (100 ml). The reaction mixture was stirred at ambient temperature for 0.5 hr and then filtered through a Millipore filter. The red-brown filtrate was concentrated under reduced pressure at 20 ml. The product crystallized as green needles. Methanol (50 ml) was added, and the product was filtered off, washed with methanol and ether, and air-dried; yield 75%.

Bis(*o*-phenylenediimine)palladium Hexafluoroantimonate, $Pd(opd)_2^+SbF_6^-$ (2). This was obtained from bis(benzonitrile)palladium chloride (**49**) in a procedure analogous to that given above for the nickel complex.

Bis(4,5-dimethyl-*o*-phenylenediimine)nickel Hexafluoroantimonate, $Ni(dmopd)_2^+SbF_6^-$ (3). This was prepared from nickel chloride (glyme) and 4,5-dimethyl-*o*-phenylenediamine in a procedure analgous to that given for $Ni(opd)_2^+SbF_6^-$ above.

Bis(*o*-phenylenediimine)nickel Bis(*cis*-ethene-1,2-dithiolato)nickelate, $Ni(opd)_2^+Ni(edt)_2^-$ (5). $Ni(opd)_2^+SbF_6^-$ (1 mmol) was dissolved in warm acetonitrile (300 ml) and treated with a solution of the tetraethylammonium salt of the bis(*cis*-ethene-1,2-dithiolato)nickel[19] anion (1 mmol) (**50**) in acetonitrile (100 ml). An immediate pre-

Table III. Analytical Data

	% calcd			% found		
Salt	C	H	N	C	H	N
1	28.44	2.39	11.06	28.65	2.36	11.16
2	25.98	2.18	10.10	25.58	2.11	9.96
3	34.14	3.52	9.96	34.14	3.48	10.00
5	37.68	3.16	10.99	36.49	2.72	10.75
6	34.44	2.89	10.04	32.27	2.62	9.60
7	31.71	2.66	9.25	28.93	2.45	8.39
8	42.44	4.27	9.90	41.49	4.20	9.66
9	53.20	4.78	13.30	53.50	4.79	13.28
10	47.25	3.30	9.18	46.76	3.30	10.48
11	48.94	3.78	8.78	48.65	3.92	9.01
12	51.89	4.64	8.97	51.54	4.57	8.07
13	48.92	3.77	8.77	48.93	3.75	8.79
14	51.88	4.64	8.07	51.86	4.61	7.97
15	49.16	3.79	8.82	48.57	3.72	8.58
16	52.11	4.66	8.11	49.90	4.53	8.11
17	43.27	3.03	16.80	43.26	2.99	16.55
18	39.38	1.98	18.37	40.49	2.14	18.28
19	43.63	2.74	19.08	42.90	2.60	18.81
20	48.37	4.06	16.92	48.45	4.08	16.88
21	55.69	4.26	13.77	56.06	4.16	12.24
22	53.58	3.15	8.32	52.20	2.87	8.16
23	55.71	3.74	12.57	56.01	3.87	14.78
24	47.21	2.07	15.74	45.44	1.92	15.53
$\mathrm{Thian^+\text{-}SbF_6^-}$	31.19	1.73		31.28	1.71	
25	43.25	1.45	10.09	43.12	1.46	10.06
26	42.95	3.21	16.70	42.61	2.82	16.81
27	47.01	3.48	6.46	45.83	3.30	6.20
28	57.65	4.13	4.98	57.47	3.79	4.75
31	30.94	0.74	10.31	30.72	0.75	10.29
32	30.63	0.76	10.21	30.39	0.97	9.02
33	30.93	0.73	10.31	30.62	0.78	10.24
34	31.14	0.75	10.38	31.64	0.94	10.33
35	28.43	0.68	9.47	28.17	0.73	8.68
36	24.73	0.59	8.23	24.61	0.69	7.59
37[a]	32.18	1.07	7.50	32.23	1.16	7.52
38	31.91	1.07	7.44	31.51	1.09	7.43
39[b]	33.60	0.00	17.42	33.74	0.22	17.32
40[c]	45.15	1.16	8.10	44.95	1.31	7.79
41	63.30	4.55	21.09	63.05	4.40	20.81
42	57.91	3.75	22.52	58.14	3.48	22.58
43	51.43	3.33	20.00	51.39	2.95	20.09

[a] Calcd: Ni, 7.86; S, 51.40. Found: Ni, 7.67; S, 51.38. [b] Calcd: S, 39.87. Found: S, 39.81. [c] Calcd: S, 37.09. Found: S, 36.7.

cipitate of a red-brown solid was obtained. This was collected by filtration, washed with acetonitrile and ether, and dried in vacuo; yield 93%.

The salts **6–20** given in Table I were obtained as dark powders in essentially quantitative yield by an analogous procedure using one of the cations described above together with the tetra-*n*-butylammonium salts of one of the following anions: bis(*o*-iminobenzenethiolato)nickel, $\mathrm{Ni(ibt)_2^-}$;[20] bis(*cis*-ethene-1,2-dithiolato)palladium, $\mathrm{Pd(edt)_2^-}$;[19] bis(toluene-3,4-dithiolato)nickel, $\mathrm{Ni(tdt)_2^-}$;[21] bis(toluene-3,4-dithiolato)cobalt, $\mathrm{Co(tdt)_2^-}$;[21] bis(toluene-3,4-dithiolato)iron, $\mathrm{Fe(tdt)_2^-}$;[21] bis(benzene-1,2-dithiolato)nickel, $\mathrm{Ni(bdt)_2^-}$;[21] bis(maleonitriledithiolato)nickel, $\mathrm{Ni(mnt)_2^-}$;[22] bis(maleonitriledithiolato)nickel dianion, $\mathrm{Ni(mnt)_2^{2-}}$.[22]

Malachite Green Bis(maleonitriledithiolato)nickelate, $\mathrm{MG^+Ni(mnt)_2^-}$ (23). A solution of Malachite Green chloride (Eastman) (2 mmol) in acetonitrile (150 ml) was treated with a solution of $(n\text{-Bu})_4\mathrm{N^+Ni(mnt)_2^-}$ (2 mmol) in acetonitrile (150 ml). Brown crystals immediately separated from solution; yield 67%. Compounds **21** and **22** were prepared in an analogous manner as gold crystals (blue powder) and a brown powder in 92% and 60% yields, respectively.

***N*-Methylphenazinium Fluorosulfate, $\mathrm{NMP^+FSO_3^-}$.** Phenazine was treated with methyl fluorosulfate in boiling $\mathrm{CH_2Cl_2}$ and the product was isolated on cooling.

***N*-Methylphenazinium Bis(maleonitriledithiolato)nickelate, $\mathrm{NMP^+Ni(mnt)_2^-}$ (24).** *N*-Methylphenazinium fluorosulfate (2 mmol) was dissolved in acetonitrile (150 ml) and treated with $\mathrm{Bu_4N^+Ni(mnt)_2^-}$ (2 mmol) in acetonitrile (150 ml). The resulting solution was cooled in the refrigerator for 24 hr and the product was isolated in 72% yield as black crystals. Compounds **27** and **28** were prepared by an analogous procedure.

Thianthrene Hexafluoroantimonate. To a well-stirred solution of thianthrene (1.08 g, 5 mmol) in a mixture of 20 ml of propionic anhydride and 160 ml of carbon tetrachloride were added, dropwise, 0.80 ml of concentrated hexafluoroantimonic acid (48% solution) (0.53 g, 6 mmol) and, then, dropwise, 0.50 ml of a "40%" solution of peracetic acid in acetic acid (approximately 3 mmol). The solution became pink on addition of the $\mathrm{HSbF_6}$ and instantly turned very dark blue on addition of the peracid. The reaction mixture was stirred for 15 min under nitrogen and then filtered through a fine glass frit, protecting the precipitate from atmospheric moisture; yield after drying (2 hr, 25°, 0.01 Torr) 60%.

Thianthrene Bis(maleonitriledithiolato)nickelate, $\mathrm{Thian^+Ni(mnt)_2^-}$ (25). Thianthrene (0.22 g, 1 mmol) was dissolved in a solution of 48% aqueous fluoroboric acid (0.15 ml) and 40% peracetic acid (0.10 ml) in acetic anhydride (50 ml), giving a deep purple solution. Tetraethylammonium bis(maleonitriledithiolato)nickelate (1 mmol) was dissolved in a minimum quantity of methylene chloride, and this solution was added to the first. A precipitate appeared which was collected by suction filtration on glass and dried under vacuum at 65°; yield 63%.

Wurster's Blue Bis(maleonitriledithiolato)nickelate, $\mathrm{WB^+Ni(mnt)_2^-}$ (26). *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine dihydrochloride (2 mmol) in methanol (50 ml) was treated with KOH (4 mmol) in water (15 ml) followed by bromine (2 mmol). A solution of $(n\text{-Bu})_4\mathrm{N^+Ni(mnt)_2^-}$ (2 mmol) in acetonitrile (50 ml) was then added. Brown crystals of the product were rapidly formed; yield 70%.

Tetrathiafulvalene Hexafluoroantimonate, $\mathrm{TTF^+SbF_6^-}$. Silver hexafluoroantimonate (0.01 mol) was dissolved in dry acetonitrile (20 ml) and added to a solution of tetrathiafulvalene (0.01 mol)[23] in acetonitrile (100 ml) with agitation. After 0.5 hr this dark red mixture was filtered through a Millipore filter and then concentrated under reduced pressure. Crystals of product were filtered off as formed, washed with methanol, and dried under vacuum; yield 80%.

Tetrathiafulvalene Bis(maleonitriledithiolato)nickelate, $\mathrm{TTF^+\text{-}Ni(mnt)_2^-}$ (31). $\mathrm{TTF^+SbF_6^+}$ (2 mmol) was dissolved in acetonitrile (100 ml) and treated with a solution of $(n\text{-Bu})_4\mathrm{N^+Ni(mnt)_2^-}$ (2 mmol) in acetonitrile (100 ml). The deep violet-brown product rapidly crystallized out of solution and was collected by filtration, washed with acetonitrile and ether, and air-dried; yield 65%.

Salts **32–38** were prepared by an analogous method using the appropriate anion. Salt **40** was similarly prepared using tetrathiotetracene acetate.[24]

Bis(dimethyl-*o*-phenylenediimine)nickel 7,7,8,8-Tetracyanoquinodimethane, $\mathrm{Ni(dmopd)_2{}^+TCNQ^-}$ (41). $\mathrm{Ni(dmopd)_2{}^+SbF_6^-}$ (5 mmol) was dissolved in warm acetonitrile (125 ml) and treated with a solution of LiTCNQ[25] (5 mmol) in methanol (20 ml). The product precipitated in 85% yield as a black microcrystalline powder.

$\mathrm{[Ni(opd)_2]_2{}^+TCNQ^-}$ (42). $\mathrm{Ni(opd)_2{}^+SbF_6^-}$ (5 mmol) was dissolved in warm acetonitrile (20 ml) and treated with a solution of $\mathrm{Li^+TCNQ^-}$ (5 mmol) in methanol (20 ml). A red-violet metallic microcrystalline precipitate rapidly formed. This was filtered off, washed with acetonitrile and ether, and dried under vacuum at 65°; yield 95%.

$\mathrm{[Pd(opd)_2]_2{}^+TCNQ^-}$ (43). $\mathrm{Pd(opd)_2{}^+SbF_6^-}$ (5 mmol) was dissolved in warm acetonitrile (400 ml) and treated with a solution of $\mathrm{Li^+\text{-}TCNQ^-}$ (5 mmol) in methanol (20 ml). A purple microcrystalline precipitate rapidly formed. This was filtered off, washed with acetonitrile, methanol, and ether, and air-dried; yield 90%.

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Registry No. **1**, 56084-60-7; **2**, 56142-82-6; **3**, 55991-06-5; **4**, 56084-61-8; **5**, 56084-62-9; **6**, 56084-69-6; 7, 56084-68-5; **8**, 55991-11-2; **9**, 55991-10-1; **10**, 56084-63-0; **11**, 56084-64-1; **12**, 55991-09-8; **13**, 56259-04-2; **14**, 56259-03-1; **15**, 56259-05-3; **16**, 56259-06-4; **17**, 55991-08-7; **18**, 56084-65-2; **19**, 56084-66-3; **20**, 55991-07-6; **21**, 55991-12-3; **22**, 55991-13-4; **23**, 55991-14-5; **24**, 55991-15-6; **25**, 55991-16-7; **26**, 55991-17-8; **27**, 55991-18-9; **28**, 56114-37-5; **29**, 53142-51-1; **30**, 53142-52-2; **31**, 55991-19-0; **32**, 55991-20-3; **33**, 56259-02-0; **34**, 56259-01-9; **35**, 55991-21-4; **36**, 55520-24-6; **37**, 55520-22-4; **38**, 55538-55-1; **39**, 55663-96-2; **40**, 55991-22-5; **41**, 55991-23-6; **42**, 56259-00-8; **43**, 56258-99-2; bis(*o*-phenylenediamine)dichloronickel, 15152-54-2; $\mathrm{Ni(opd)_2}$, 55991-48-5; Thian$^+$SbF$_6^-$, 55991-24-7; TTF$^+$SbF$_6^-$, 55991-25-8.

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On the Stability of Thallium(I) Transition Metal Carbonyls. Substitution Reactions of Thallous Tetracarbonylcobaltate

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The reactions of $TlCo(CO)_4$ with a variety of Lewis bases in noncoordinating solvents proceed to completion in several hours at room temperature with gas evolution and formation of either $TlCo(CO)_3L$ or $Tl[Co(CO)_3L]_3$ and thallium metal. Thallium(I) compounds stable in solution at room temperature are formed with those Lewis bases which give substituted cobalt carbonyl anions of relatively low basicity ($pK_a < 5$). In particular, $TlCo(CO)_3P(OC_6H_5)_3$ and $TlCo(CO)_3P(p\text{-}OC_6H_4Cl)_3$ result from the reaction of the corresponding Lewis bases with $TlCo(CO)_4$. With ligands giving more strongly basic anions, thallium(III) derivatives and thallium metal form. Lewis bases including $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, and $P(n\text{-}C_4H_9)_3$ which give substituted hydriodocobaltcarbonyl derivatives with pK_a's of greater than 5 yield thallium metal and thallium(III) derivatives of $Co(CO)_3L^-$. These substitution reactions suggest that a pK_a of about 5 for the hydridocarbonyl is the upper limit of the base strength of the corresponding metal carbonyl anion which is consistent with the formation of thallium(I) derivatives which are stable in noncoordinating solvents.

Introduction

At the beginning of this work, thallium(I) transition metal carbonyls were not well known. Only one such compound, $TlCo(CO)_4$, had been well characterized[1,2] although brief reports of $Tl[C_5H_4CH(C_6H_5)_2Cr(CO)_3]$[3] and $Tl[C_5H_5M(CO)_3]$ (M = Mo[4] and W[5]) appeared in the literature. Of these, the molybdenum compound was reported to decompose even in the solid state, and the tungsten derivative had only been mentioned in a patent. Attempts to prepare $TlMn(CO)_5$[6,7] by the metathetical reaction of a thallium(I) salt with the metal carbonyl anion had resulted in the formation of the corresponding thallium(III) derivative. The substitution reaction of $TlCo(CO)_4$ with triphenylphosphine also gave a thallium(III) compound, $Tl[Co(CO)_3P(C_6H_5)_3]_3$.[2]

Toward the end of this study, Burlitch[8] reported the preparation of $Tl[C_5H_5M(CO)_3]$ (M = Cr, Mo, and W), $TlMn(CO)_5$, and $TlCo(CO)_3P(C_6H_5)_3$. The group 6B derivatives were isolated and characterized, but were only stable in 10% aqueous sodium hydroxide or in the solid state at −65°. In other solvents such as tetrahydrofuran and toluene, these compounds decomposed more or less rapidly to the corresponding thallium(III) derivatives and thallium metal. $TlCo(CO)_3P(C_6H_5)_3$ and $TlMn(CO)_5$ were only detected in solution and were characterized by infrared spectroscopy. $TlMn(CO)_5$ was generated in tetrahydrofuran at −65° and was stable under these conditions. However, at room temperature, it rapidly decomposed to $Tl[Mn(CO)_5]_3$ and tallium metal. A similar decomposition took place for $TlCo(CO)_3P(C_6H_5)_3$ in a tetrahydrofuran–methanol solution at room temperature.

From these observations, it appeared with the exception of $TlCo(CO)_4$ and, perhaps, $Tl[C_5H_4CH(C_6H_5)_2Cr(CO)_3]$ that thallium(I) transition metal carbonyls were unstable with respect to disproportionation to the corresponding thallium(III) derivatives and thallium metal.

We have examined the reactions of a variety of Lewis bases with $TlCo(CO)_4$ in order to explore the question of the general instability of $TlCo(CO)_3L$ and to develop a convenient route for the preparation of the corresponding thallium(III) derivatives. During this study we have prepared several new thallium(I) metal carbonyl derivatives and have determined the conditions under which additional stable thallium(I) derivatives can be prepared.

Experimental Section

All operations were conducted under nitrogen using Schlenk-type equipment with deoxygenated solvents. Tetrahydrofuran was distilled from lithium aluminum hydride and stored over molecular sieves. All spectra were recorded on a Perkin-Elmer 221 spectrophotometer with NaCl optics. The spectra were calibrated in the carbonyl region using polystyrene and $Hg[Co(CO)_4]_2$ in heptane. The CO frequencies of this solution were taken from Adams.[9] Melting points were determined in sealed capillary tubes under a nitrogen atmosphere. The compounds