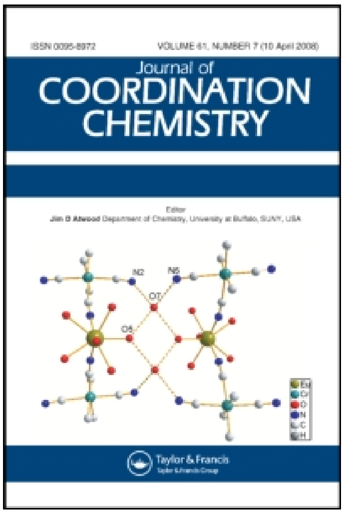

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STUDIES OF INTERMOLECULAR INTERACTIONS IN PLANAR METAL COMPLEXES III[1] BIS(ETHYLENE-1,2-DITHIOLENE) COMPLEXES OF NICKEL, PALLADIUM, AND PLATINUM

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The synthesis and characterization of nineteen new bis-dithiolene metal complexes of the type $A_n{}^+[MS_4C_4H_4{}^{n-}]$, where A^+ = various organic cations, M = Ni, Pd, Pt, and n = 0, 1, are described. The results of redox, infrared, electronic spectral, and NMR measurements on these complexes support a monomeric, planar structure for the complex units both in solution and, with the exception of the neutral $MS_4C_4H_4$ (M = Pd, Pt) derivatives, in the solid state. However, evidence for intermolecular interactions in these solids has been found on the basis of four-probe conductivity measurements. The conductivities of these complexes range from less than 10^{-10} ohm^{-1} cm^{-1} to $\sim 10^{-5}$ ohm^{-1} cm^{-1} and depend markedly on the nature of A^+, M and *n*. On the basis of these measurements, empirical generalizations relating conductivity and the structural parameters A^+ and M are derived. In addition, information regarding the dependence of the conductivity on the spacial relationship of the complex units in the solid is obtained from measurements on single crystals of $NiS_4C_4H_4$ and $PtS_4C_4H_4$ as a function of crystallographic direction. The implications of these results with regard to the electron transport mechanism in such solids are discussed.

INTRODUCTION

Considerable attention has been focused recently on the unusual electrical properties exhibited by certain square-planar metal complexes. For example, the d^8 metal complexes, $Pt(NH_3)_4PtCl_4$ and $Ir(CO)_2(acac)$, have been found to exhibit highly directional conductivity behavior with room temperature electrical conductivities as high as 10^{-2} ohm^{-1} cm^{-1} in the preferred conductivity direction.[2,3] Although the metal dithiolene complexes, $M(S_2C_2R_2)^{n-}{}_{2,3}$, where M = Ni, Pd, Pt, Mo, Fe, Cu, V, W, Re, Cr, Co and R = CN, CH_3, CF_3, C_6H_5, etc, are probably best known for their unique molecular properties, such as their reversible redox behaviour and highly delocalized ground state electronic configuration,[4] several bis- and tris-complexes of this type have also been found to exhibit significant electrical conductivity in the solid state.[5] In contrast to the aforementioned d^8 metal complexes, where direct metal-metal interactions are possible and the ligand groups apparently only moderate these interactions, it is likely that in the bisdithiolene complexes the extended π-electron system of the molecular units plays an important role in the electron transport process.

The present investigation centers on complexes of the unsubstituted ethylenedithiolate ligand, $H_2C_2S_2{}^{2-}$, of the type $A_n{}^+[MS_4C_4H_4{}^{n-}]$ where A^+ = monopositive cation, M = Ni, Pd, Pt, and n = 0,1. These complexes were chosen for study because of the small size of the hydrogen substituent on the ligand and the availability of stable oxidation states with low net charge, thus facilitating both close intermolecular packing and electron transfer between complex units. Following the synthesis of the $H_2C_2S_2{}^{2-}$ ligand in 1964,[6] a number of neutral and monoanionic bis- and tris-complexes were described.[7,8] With the exception of the $NiS_4C_4H_4{}^{n-}$ complexes, however, little additional information on bis complexes of this ligand has been reported. The recent synthesis of the $[MS_4C_4H_4]$, M = Pd and Pt, compounds and the discovery of their unusual dimeric structure[9,10] has generated renewed interest in these materials. We now wish to report the full details regarding their molecular properties and electrical conductivity in the solid state.

EXPERIMENTAL

Starting Materials

Sodium ethylene-1,2-dithiolate ($Na_2S_2C_2H_2$) was prepared by the method of Schroth and Peschel[6] and stored in a N_2-filled dry-box until used.

Tetrachloroplatinate (II) and tetrachloropalladate (II) were obtained from Matthey Bishop and Research Organic/Inorganic Chemicals as the anhydrous salts. All other chemicals were of reagent grade quality and were used without further purification.

Preparation of Complexes

$A^+[MS_4C_4H_4^-]$ Complexes: Method I. The $A^+[MS_4C_4H_4^-]$ complexes were generally prepared by direct reaction of $Na_2S_2C_2H_2$ with a stoichiometric amount of nickel chloride, sodium tetrachloropalladate (II), or sodium tetrachloroplatinate (II) at approximately $-15°C$.[11] The reaction was allowed to proceed for a few minutes in the case of nickel, 4–6 hours for palladium, and overnight for platinum before an excess of the appropriate cation, A^+, as the halide salt was added. Nickel and platinum mixtures were allowed to react overnight, and the palladium mixtures for 4–6 hours before the crude product was filtered off, washed with water and air-dried. The $A^+[MS_4C_4H_4^-]$ product was then extracted with acetone and the extract evaporated to dryness. After purification by precipitation from acetone solution with benzene, the products were obtained as dark solids in yields ranging from 80–90% for nickel complexes to 10–30% for palladium complexes to 20–45% for platinum complexes.

$A^+[MS_4C_4H_4^-]$ Complexes: Method II. Several of the nickel and platinum complexes were prepared from the $CsMS_4C_4H_4$ derivative by reaction with an excess of the salt A^+X^-, where X = Cl or Br, in acetonitrile solution. After removing the precipated CsX by filtration, the solution was evaporated to dryness and the residue washed well with water to remove the excess A^+X^- salt. The crude product was then recrystallized from acetonitrile to yield the $[A^+][MS_4C_4H_4^-]$ complex in 80–95% yield.

Attempts to prepare the following compounds by the above methods were unsuccessful: $[A^+][MS_4C_4H_4^-]$ where M = Ni and $[A^+]$ = N-methyl-phenazinium; M = Pd and $[A^+]$ = N-methylphenazinium, cesium, methyl-pyridinium, quinolinium, and morpholinium; M = Pt and $[A^+]$ = N-methylphenazinium, quinolinium, and morpholinium. Also, efforts to grow single crystals of the $A^+MS_4C_4H_4^-$ compounds suitable for use in conductivity measurements were not successful.

$[MS_4C_4H_4]^0$ Complexes, M = Ni,Pd,Pt; These complexes were prepared by oxidation of $[(n\text{-}C_3H_7)_4N^+][MS_4C_4H_4^-]$ with I_2 in CH_3CN solution. Equimolar amounts of $[(n\text{-}C_3H_7)_4N^+][MS_4C_4H_4^-]$ and I_2 were dissolved in minimum amounts of CH_3CN and the solutions were filtered before being mixed at room temperature. The reaction mixture was evaporated to one-half its volume and the crude product was collected by filtration, washed with CH_3CN, and air-dried. Recrystallization from CS_2 gave the purified complex as a dark solid in yields ranging from 60% to 70% for $NiS_4C_4H_4$ and $PtS_4C_4H_4$ to<10% for $PdS_4C_4H_4$. Single crystals of $NiS_4C_4H_4$ and $PtS_4C_4H_4$ were grown from CS_2 solution by slow evaporation. The $NiS_4C_4H_4$ crystals were obtained as large, thick needles, up to 5 mm long and 0.8 mm by 0.5 mm in cross section. The samples used for electrical measurements were all cut from one particularly large crystal and measured approximately $0.8 \times 0.7 \times 0.4\ mm^3$ with approximate 90° angles between crystal edges. Single crystals of $PtS_4C_4H_4$ were typically $\sim 0.2 \times 0.2 \times 0.5\ mm^3$. Elemental analyses of the compounds prepared in this work are given in Table I.

Electrical Measurments: A four-electrode DC conductivity technique was used to measure the electrical conductivity of polycrystalline samples in the form of pellets pressed at 85,000 psi. Electrical contact to the sample was made with 5 mil platinum wires attached with silver conducting paste. Voltage measurements were made using a Keithley 610C electrometer. Measurements were carried out *in vacuo* at pressures $<10^{-5}$ torr, or, in the case of the $NiS_4C_4H_4$ single crystals, under an atmosphere of dry N_2, as a function of temperature. Conductivity measurements on $NiS_4C_4H_4$ single crystals were made using the same four-probe technique. In the case of $PtS_4C_4H_4$ single crystals, a two probe AC technique using a Model B224, Wayne-Kerr AC Bridge for direct measurement of sample resistance was employed due to the small size of the available crystals.

Activation energies for conduction were determined from log σ vs 1/T plots, according to eq. 1

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{1}$$

where σ = conductivity, E_a = thermal activation energy for conduction, and T = absolute temperature. Such plots yielded straight lines, whose slope and intercept were determined by the least squares method.

X-ray Data: X-ray powder diffraction measurement were made for each series of compounds using $CuK\alpha$ radiation and 12-hour exposures. In

TABLE I

Analytical Data for new $[A^+]$ $[MS_4C_4H_4]^{0}{}_{,}{}^{-1}$ Complexes

$[A^+]$	M	%C		%H		%N		%S	
		calc	found	calc	found	calc	found	calc	found
	Pd	16.8	18.3	1.41	1.61	—	—		
—	Pt	12.8	13.0	1.07	1.10	—	—	34.2	34.3
N-methylquinolinium	Ni	43.9	43.6	3.68	3.55	3.65	3.62	33.5	33.3
	Pd	39.0	39.3	3.27	3.27	3.25	3.03		
	Pt	32.4	32.9	2.72	2.74	2.70	2.53		
tetra-n-propylammonium	Ni	45.2	45.1	7.58	7.34	3.29	3.28		
	Pd	40.6	40.8	6.82	7.00	2.96	2.80	27.1	26.9
	Pt	34.2	33.8	5.74	5.63	2.49	2.30	22.8	22.7
tetraphenylphosphonium	Ni	58.1	58.6	4.18	4.15	—	—	22.2	22.0
	Pd	53.7	53.3	3.86	3.90	—	—	20.5	20.7
	Pt	47.1	46.8	3.38	3.35	—	—	17.9	18.1
triphenylmethylphosphonium	Ni	53.5	53.6	4.29	4.30	—	—	24.8	25.3
	Pd	49.0	48.8	3.93	4.00	—	—		
	Pt	43.3	42.1	3.40	3.40	—	—		
cesium	Ni	12.9	12.8	1.08	1.08	—	—		
	Pt	9.5	9.8	0.79	0.88	—	—	25.2	25.5
methylpyridinium	Ni	36.1	35.9	3.63	3.50	4.20	5.00		
	Pt	25.6	25.7	2.58	2.50	2.98	3.00		
quinolinium	Ni	42.3	42.3	3.28	3.29	3.79	4.12		
morpholinium	Ni	29.4	28.3	4.31	4.00	4.28	4.14		

addition, one of the crystal segments used in the $NiS_4C_4H_4$ single crystal conductivity measurements was examined by x-ray precession techniques to determine the relationship between the conductivity and crystallographic directions.

Spectral and Redox Measurements

Infrared spectra were obtained using a Perkin-Elmer Model 457 Infrared Spectrophotometer. Solid samples were run as Nujol mulls and solution spectra were obtained using fixed path length KBr solution cells and spectral grade solvents. Electronic spectra were measured using a Cary Model 14 Spectrophotometer. NMR spectra of the $MS_4C_4H_4$ complexes were recorded on a Varian XL-100 Spectrometer in carbon disulfide solution.

Redox data were obtained in acetonitrile solution by cyclic voltammetry using a 0.0100 platinum wire working electrode and a Ag/AgCl reference. The solutions used were 1mM in both the $MS_4C_4H_4$ and $MS_4C_4H_4{}^{-1}$ complexes, except for M = Pd, where due to limited solubility of the $PdS_4C_4H_4$ complex, $PdS_4C_4H_4{}^{-1}$ alone was used. The solutions also contained 0.2 M $(C_6H_5)_4PCl$ as supporting electrolyte. The formal electrode potentials were obtained as the midpoint between the anodic and cathodic peaks. The peak separation in each case was close to 57 mV, which is consistent with reversible behavior.

RESULTS

Characterization of these compounds as bis-dithiolene complexes of the general type $A^+{}_n$ $[MS_4C_4H_4]_n{}^{n-}$ where A^+ = cation, M = Ni, Pd, Pt, $n = 0,1$, rests on the results of analytical data (Table I) and on NMR, infrared, and electronic spectral data. Because of the interest in the solid state properties of these complexes,[12] and the sensitivity of these properties to changes in A^+, a broad range of cationic derivatives was chosen for study.

The new $MS_4C_4H_4$ (M = Pd, Pt) complexes were obtained as black solids which were only slightly soluble in solvents such as CS_2, benzene and $CHCl_3$, in the solubility order Pt $\gg$ Pd. The very limited solubility of $PdS_4C_4H_4$, and to a lesser extent PtS_4H_4, is understandable in terms of the dimeric structure of these two compounds in the solid state.[10] Molecular weight measurements for $PtS_4C_4H_4$ show this compound to be monomeric in both benzene and $CHCl_3$ solutions; $PdS_4C_4H_4$ was insufficiently soluble to permit the determination of its molecular weight. This large difference in solubility among the $MS_4C_4H_4$ (M = Pd, Pt) complexes is rather surprising in view of their otherwise close chemical and structural similarity. It is possible that this reflects a corresponding difference in the respective dimer binding energies, with $(PdS_4C_4H_4)_2$ as the more tightly bound species.

Proton nmr spectra were obtained for both $NiS_4C_4H_4$ and $PtS_4C_4H_4$ in CS_2 solution. The $NiS_4C_4H_4$ complex gave a single sharp line at $\tau = 1.4$ ppm relative to TMS, close to the value previously reported by Schrauzer and Mayweg ($\tau = 0.8$ ppm).[8] The $PtS_4C_4H_4$ complex gave a three line nmr spectrum with the most intense peak at a chemical shift value identical to that of $NiS_4C_4H_4$. Two considerably weaker lines were observed at ±103 cps from this central peak, presumably arising from Pt^{195}-H spin-spin coupling. These observations are consistent with the expected delocalized D_{2h} structure for the monomeric $MS_4C_4H_4$ complexes in solution. The apparent identity of the chemical shift values for the $NiS_4C_4H_4$ and $PtS_4C_4H_4$ protons indicates that the metal does not play a large role in determining the electron distribution at the periphery of the chelate ring in these complexes.

Redox potentials were determined by cyclic voltammetry. The results, summarized in Table II, are in agreement with previous data for the M = Ni, Pd cases ($E_{\frac{1}{2}} = +0.120$ and $+0.165$ volts, respectively);[13] no previous data were found in the case of the Pt derivative.

TABLE II

Redox potentials in CH_3CN solution

$[MS_4C_4H_4]^\circ + e^- \rightleftarrows [MS_4C_4H_4]^-$ (volts)

M	$E_{1/2}$
Ni	+ .11
Pd	+ .17
Pt	+ .10

Infrared spectra of the $[MS_4C_4H_4]^{0,\ 1}$ complexes were obtained in the solid state as Nujol mulls and, where permitted by solubility and solvent transparency, in CS_2 and CH_3CN solution. A summary of infrared spectral bands is given in Tables III and IV. Assignments have been made on the basis of recent normal coordinate treatments of $MS_4C_4(CH_3)_4$ complexes, where M = Ni, Pd, and Pt, and of $NiS_4C_4H_4$.[14,15]

The positions of the observed electronic transitions, along with tentative assignments, are summarized in Table V. Assignments were made with the aid of the energy level diagram derived from a recent molecular orbital treatment of $NiS_4C_4H_4$ by Schrauzer and Mayweg[8] and by analogy to previous assignments for the $NiS_4C_4H_4{}^{n-}$ complexes.[8]

X-ray powder diffraction data for each compound were collected in order to determine the structural

TABLE III

Infrared Spectra[a] of $[MS_4C_4H_4]^{0,-1}$ Complexes (in cm^{-1})

$NiS_4C_4H_4$	$NiS_4C_4H_4{}^{-1b}$	$PdS_4C_4H_4$	$PdS_4C_4H_4{}^{-1c}$	$PtS_4C_4H_4$	$PtS_4C_4H_4{}^{-1b}$	Assignment
1340 vs	1420^d m	1342 s	1395^d vs	1353 vs	1409^d vs	ν (C—C)
1330 s				1341 m		
		1302^d m				δ (C—H)
1290 s	1276 w	1296^d m	1276^d m	1296 m	1275^d s	
1260 m		1131^d m		1278 w		
1099 vs	1105 m	1119^d s	1112^d vs	1111s	1117 s	
		883^d w				δ (C—H) and ν (C—S)
		878^d m				
		878^d m				
874 m	825 s	872^d s	831^d s	878 m	828 s	
799 w	699 w	790^d w	715^d w	880^d w	752^d w	ν (C—S)
753 vs	719 vs	753^d s	705^d w	750 s	707 vs	out-of-plane C—H bend
720 vs	694 s	742^d m	690^d vs	714 s	695 s	ν (C—S) and ring def.
625^d w	669^d w	625^d w	669^d w	635^d w	670^d w	
427^d m	418^d s	418^d w	398^d w	408^d m	419^d m	unassigned
		390^d w		379^d m		ν (M—S)?
309^d m	303^d m	335^d m	355^d m	339^d m	363^d m	
		320^d m	347^d m	328^d m	350^d m	
278^d w		279^d w	281^d m	279^d m	283^d m	ring def.

[a] Neutral complexes in CS_2 solution; monoanionic complexes in CH_3CN solution.
[b] As the Cs^+ salt
[c] As the $(n\text{-}C_3H_7)_4N^+$ salt
[d] Solid state, nujol mull value

relationship between the various $A^+[MS_4C_4H_4{}^{n-}]$ complexes. For the neutral complexes, there was a clear difference between the diffraction pattern for $NiS_4C_4H_4$ on the one hand, and $PdS_4C_4H_4$ and $PtS_4C_4H_4$ on the other; this observation was later explained by single crystal structure studies which showed the compound where M = Ni to have a planar, monomeric molecular structure and the compounds where M = Pd, Pt to have a dimeric structure.[7] For the monoanionic complexes, each of the derivatives of a particular cation was found to be isomorphous.

Typical conductivity vs 1/T curves for an isomorphous series of bis-dithiolene complexes are shown in Figure 1. The results of four point probe

TABLE IV

Comparison of solid state[a] and solution[b] $MS_4C_4H_4$ infrared spectra

ν (C—C) cm^{-1}

	solid	solution
$NiS_4C_4H_4$	1343 s, 1308 s	1340 vs, 1330 s
$PdS_4C_4H_4$	1386 s	1342 s
$PtS_4C_4H_4$	1392 vs	1353 vs, 1341 m
	δ (C—H) and ν (C—S)	
$NiS_4C_4H_4$	827 s	874 m
$PtS_4C_4H_4$	872 s	878 m
	ν (C—S) and ring def.	
$NiS_4C_4H_4$	725 s, 717 s	720 s
$PtS_4C_4H_4$	730 m	714 s

[a] Nujol mull
[b] CS_2 solution

TABLE V

Electronic Spectra[a] of $[MS_4C_4H_4]^{0,-1}$ Complexes (in cm^{-1})

$NiS_4C_4H_4$	$PdS_4C_4H_4$	$PtS_4C_4H_4$	$NiS_4C_4H_4{}^{-1}$	$PdS_4C_4H_4{}^{-1}$	$PtS_4C_4H_4{}^{-1}$	Assignment
13,870[b]	12,740(9490)[c]	14,720(26000)	11,696(6367)	9091(9267)	11,494(8460)	$2b_{1u} \rightarrow 3b_{2g}$
			15,700(351)		17,544(358)	$2b_{1u} \rightarrow 3b_{2g}$
18,080(22000)	18,520(1760)[c]	19,490(2630)[d]	19,310(1670)[d]		19,607(627)[d]	$2b_{2u}, 2b_{3u}, 2b_{1g} \rightarrow 3b_{2g}$
		20,240(2890)	19,840(1910)		21,322(2700)	$2b_{2u}, 2b_{3u}, 2b_{1g} \rightarrow 3b_{1g}$
22,220(7500)[d]	27,780(700)[d,e]	23,530(764)[d]	20,450(890)[d]		23,697(1010)[d]	$2a_g \rightarrow 3b_{2g}$
			22,940(695)[d]		26,667(1865)	$2a_g \rightarrow 3b_{1g}$
26,460(18400)	29,850(2300)[e]	30,120(1163)[d]	28,570(3780)[d]		33,330(953)[d]	$2b_{3g} \rightarrow 2a_u$
						$1a_u \rightarrow 3b_{2g}$
						$2b_{2g} \rightarrow 2a_u$
33,360(21400)[d]	31,950(4310)[d, e]	35,590(4894)	32,470(13,700)		37,736(7700)[d]	$1a_u \rightarrow 3b_{1g}$
36,360(21400)[d]	40,100	44,640(41667)	40,000(15,500)		44,444(35000)	$2b_{1u} \rightarrow 3b_{3g}$
			48,310(22800)		47,170(32100)	$2b_{2u}, 2b_{3u}, 2b_{1g} \rightarrow 3b_{3g}$
			23,980(1480)[d]		27,248(1865)	$2b_{2g} \rightarrow 2a_u$
					14,535(539)	—
					14,881(480)	—

[a] Neutral complexes in ether solution; monoanionic complexes in CH_3CN solution; extinction coefficients are given in paretheses.
[b] Data from ref. 8. [c] CS_2 solution. [d] Shoulder. [e] Benzene solution.

TABLE VI

Solid State Electrical Conductivity[a] of $MS_4C_4H_4{}^{0,-1}$ and TCNQ[b] Complexes

	M = Ni		M = Pd		M = Pt		TCNQ	
A^+	σ (Ω^{-1}cm^{-1})	E_a (eV)	σ (Ω^{-1}cm^{-1})	E_a (eV)	σ (Ω^{-1}cm^{-1})	E_a (eV)	σ (Ω^{-1}cm^{-1})	E_a (eV)
—	7.5×10^{-6}	0.33	1.6×10^{-0}	0.28	$< 10^{-10}$	[c]	[d]	
cesium	1.4×10^{-7}	0.46	[d]		8.3×10^{-7}	0.42	5×10^{-4}	0.18
quinolinium	1.3×10^{-7}	0.26	[d]		[d]		10^{-5}	[c]
methylpyridinium	3.3×10^{-10}	1.29	[d]		8.7×10^{-9}	1.00	10^{-5}	[c]
methylquinolinium	5.0×10^{-10}	0.44	1.8×10^{-9}	0.42	1.0×10^{-7}	0.38	1×10^{-7}	[c]
morpholinium	1.9×10^{-8}	0.48	[d]		[d]		1×10^{-9}	0.32
tetra-n-propylammonium	$< 10^{-10}$	[c]	$< 10^{-10}$	[c]	$< 10^{-10}$	[c]	6.3×10^{-10}	0.87
triphenylmethylphosphonium	4.2×10^{-9}	0.74	1.4×10^{-9}	0.11	3.5×10^{-10}	0.28	2×10^{-11}	[c]
tetraphenylphosphonium	$< 10^{-10}$	[c]	$< 10^{-10}$	[c]	$< 10^{-10}$	[c]	[d]	

[a] at 300°K
[b] at room temperature; ref. 16, pp. 732 ff.
[c] activation energy not determined
[d] compound was not available

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DC conductivity measurements as a function of temperatures are summarized in Table VI. Also included are conductivity and activation energy data, where available, for the corresponding $A^+(TCNQ^-)$ salts. The results of single crystal conductivity measurements are summarized in Table VII.

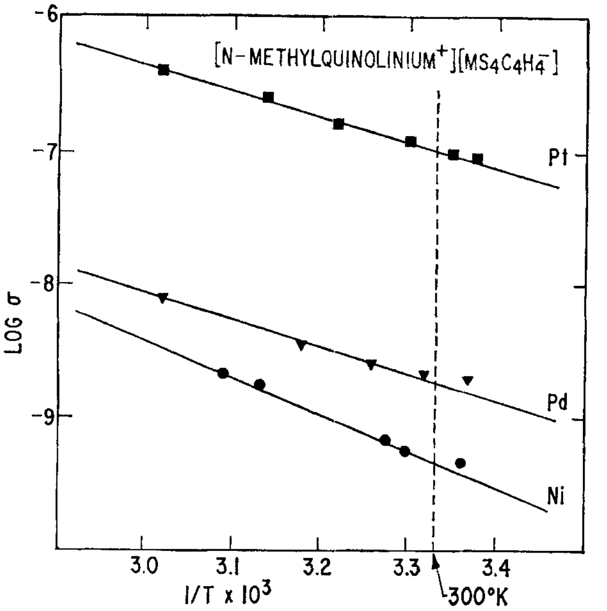

FIGURE 1 Log σ vs. 1/T plot for (N-methylquinolinium][$MS_4C_4H_4$] complexes

TABLE VII

Single Crystal Electrical Conductivity[a] of $NiS_4C_4H_4$ and $PtS_4C_4H_4$

Complex	Crystal Direction	σ ($\Omega^{-1}cm^{-1}$)	E_a (eV)
$NiS_4C_4H_4$	010, needle axis	7.1×10^{-6}	0.23
$NiS_4C_4H_4$	101	1.1×10^{-6}	$\geqslant 0.10$[b]
$NiS_4C_4H_4$	345	2.0×10^{-6}	0.24
$PtS_4C_4H_4$	010, needle axis	1.9×10^{-9}	—
$PtS_4C_4H_4$	⊥ to needle axis	7.3×10^{-10}	—

[a] at 300°K

[b] poor thermal contact for the crystal in this orientation is likely; therefore, the true activation energy value is probably greater than indicated.

DISCUSSION

The results of spectral and redox measurements are consistent with the description of the $A^+[MS_4C_4H_4{}^{n-}]$ M = Ni, Pd, Pt, n = 0,1, complexes in terms of planar and largely unassociated $MS_4C_4H_4{}^{n-}$ ($n = 0,1$) units in solution, quite analogous to the corresponding $A_n^+[MS_4C_4R_4{}^{n-}]$ complexes, where R = CH_3,CN,C_6H_5, etc.[4] Specifically, the new electronic spectral results for the $[MS_4C_4H_4{}^{n-}]$, M = Pd, Pt, $n = 0,1$ species are consistent with those previously found for the $NiS_4C_4H_4{}^{n-}$ and other bis-dithiolene complexes and can be explained in an analogous manner on the basis of the MO scheme of Schrauzer and Mayweg.[8] Also, the infrared bands in the C–C, C–S, and M–S stretching regions for the $A^+{}_n[MS_4C_4H_4]^{n-}$ derivatives closely resemble those previously observed for other bis-dithiolene complexes, and show similar shifts upon variation of the metal (M) and oxidation state (n-).[4,15] No significant dependence of the infrared spectrum on either the nature of the cation, A^+, or the medium in which the spectrum was run (i.e., in the solid state as a Nujol mull or in solution) was found for any of the $A^+[MS_4C_4H_4{}^-]$ complexes. On the other hand, inspection of the infrared spectra of the neutral $MS_4C_4H_4$ complexes reveals significant shifts in several band positions between the solid and solution states for $PdS_4C_4H_4$ and $PtS_4C_4H_4$, but not for $NiS_4C_4H_4$.

Table IV summarizes some of the band shifts which are observed when the $MS_4C_4H_4$ compounds are dissolved in CS_2. Whereas shifts of only a few cm^{-1} are observed in the case of $NiS_4C_4H_4$, relatively large shifts in certain of the absorption bands are observed for $PdS_4C_4H_4$ and $PtS_4C_4H_4$. Indeed, the spectra of all three complexes in CS_2 solution are very similar; whereas in the solid state the spectra of $PdS_4C_4H_4$ and $PtS_4C_4H_4$ are quite similar to each other but different in some respects from the $NiS_4C_4H_4$ spectrum. These observations are consistent with the results of recent x-ray structure determinations which show $NiS_4C_4H_4$ to be a planar, monomeric molecule, whereas $PdS_4C_4H_4$ and $PtS_4C_4H_4$ are metal-metal bonded dimers.[10] These dimeric structures consist of two approximately planar $MS_4C_4H_4$ units with bond distances and angles similar to those in the monomeric structure; consequently, the similarities which do exist between spectra for the monomer and dimers are also understandable. The fact that all three complexes have similar infrared spectra in CS_2 solution suggests that all are monomeric in solution. This observation is supported by the molecular weight data which show $NiS_4C_4H_4$ and $PtS_4C_4H_4$ to be monomeric in both $CHCl_3$ and benzene.

Thus, these measurements provide no indications of appreciable intermolecular interactions, either in the solid or solution states, with the exception of the dimerization of $PdS_4C_4H_4$ and $PtS_4C_4H_4$ in the solid. Even in these latter cases no unusually short intermolecular contacts between dimer units were found.[10] On the other hand, clear evidence for the existence of such intermolecular interactions among the $A_n^+[MS_4C_4H_4{}^{n-}]$ complexes in the solid state is evidenced by the results of electrical conductivity measurements.

The conductivities and activation energies of the $A_n^+[MS_4C_4H_4{}^{n-}]$ complexes cover a wide range of values, from greater than $10^{-6}\Omega^{-1}\,cm^{-1}$ to less than $10^{-10}\Omega^{-1}\,cm^{-1}$ and from 0.11 ev to 1.29 ev, depending on the nature of M, n, and A^+. Among the isomorphous series of monoanionic complexes with a given cation, A^+, there appears to be a general trend of increasing conductivity with metal, in the order Ni<Pd<Pt. For example, the conductivities of N-methylquinolinium compounds increase from $5.0 \times 10^{-10}\ \Omega^{-1}\,cm^{-1}$ for $M = Ni$ to $1.8 \times 10^{-9}\ \Omega^{-1}\,cm^{-1}$ and $1.0 \times 10^{-7}\ \Omega^{-1}\,cm^{-1}$ for $M = Pd$ and $M = Pt$, respectively. The only exceptions to this trend are among the complexes of very low conductivity ($<10^{-8}\ \Omega^{-1}\,cm^{-1}$), where uncertainty in the measurements may exceed the small differences observed, and in the case of the neutral $MS_4C_4H_4$ complexes which, for structural reasons, constitute a special case. This trend may be understood by considering the relative size of the valence orbitals in the isoelectronic d^8 series of group VIII metals. Platinum, with its larger 5d and 6p valence orbitals may be expected to provide better intermolecular orbital overlap than palladium or nickel.

Previous evidence for intermolecular interactions involving the metal atom in bis-dithiolene compounds comes from several crystal structure studies which indicate possible metal-sulfur interactions between planar anion units. For example the $[\phi_3ClP^+][AuS_4C_4(CF_3)_4{}^-]$ structure consists of separate stacks of cations and anions. The anion units, with square-planar coordinated gold, stack in a configuration such that the shortest intermolecular contacts, at 3.96Å, are between gold and sulfur atoms.[17] A similar situation occurs in the $[Bu_4N^+][CuS_4C_4(CN)_4^-]$ structure, where the shortest intermolecular contacts are at 3.7Å and involve copper and sulfur atoms.[18] Pairs of anion units are stacked in a staggered manner in this case, so that there are alternating Cu-Cu distances of 4.03Å and 4.43Å. A third case is that of $[\phi_3MeP^+][NiS_4C_4(CN)_4{}^-]$ where a pairwise interaction between nickel and sulfur is indicated both by structure determination[11] and by magnetic measurements.[19] The anion units stack in columns with alternating distances of 3.41Å and 3.56Å between molecular planes. The minimum intermolecular nickel-sulfur contacts here are 3.59Å, whereas that between metal atoms is 4.4Å. Magnetic measurements for this compound also indicate a pairwise interaction resulting in a reduction in the magnetic moment of nickel from the expected value.

The activation energies for conduction in the $MS_4C_4H_4{}^{-1}$ complexes are also metal dependent, and in general decrease with metal in the order $Ni < Pd < Pt$. For example, in the N-methylquinolinium series, the activation energy decreases from 0.44 ev for $M = Ni$ to 0.42 ev and 0.38 ev for $M = Pd$ and $M = Pt$ respectively. Thus, if we presume that the conductivity and activation energy are related by the equation, $\sigma = \sigma_0 e^{-E_a/kT}$, where σ is the conductivity at temperature T, E_a is the activation energy and σ_0 is, to the first approximation, temperature independent and roughly proportional to mobility,[20] it is apparent that the conductivity trend observed for the isomorphous $A^+MS_4C_4H_4^-$ complexes is, at least in part, a reflection of a change in the activation energy for electron transport. However, the magnitude of the activation energy change is, in general, insufficient to account for the large variation in conductivity observed and it is probable that both mobility and activation energy differences contribute to the observed trend.

These observations and, in particular, the inverse relationship between activation energy and conductivity provide an interesting contrast to earlier work on organic molecular compounds where the reverse trend has been noted in a large number of cases.[21] This may indicate that the conduction mechanism in the bis-dithiolene complexes is basically different from that in these organic systems where a mechanism involving the tunneling of electrons through non-transparent intermolecular barriers has been proposed to account for the data obtained.[21]

In the case of the neutral $MS_4C_4H_4$ complexes, the dependence of conductivity upon the metal is rather different. Here, the nickel complex is considerably more conductive than its Pd and Pt analogs, which are both close to the lower limit of measurability by our four-electrode conductivity measurement technique. Indeed, the $NiS_4C_4H_4$ complex is one of the most conductive bis-dithiolene complexes yet studied[5] and is almost an order of magnitude higher than any of the $[A^+][MS_4C_4H_4^-]$ complexes. It was this unusual difference in conductivity behavior that led to the recent structure determinations of the three $MS_4C_4H_4$ complexes and the identification of the dimeric nature of the Pd and Pt derivatives.[10, 22] The substantial difference in the molecular and crystal structures of the Pd and Pt complexes as compared to the nickel derivative could certainly account for the anomalous variation in conductivity with the metal noted for this series.

It is interesting to note that the results obtained for $NiS_4C_4H_4$ and $PtS_4C_4H_4$ in polycrystalline form are in reasonably good agreement with those obtained on single crystals (see Table VII). Crystals of these two compounds which were of suitable size and quality for conductivity measurements were obtained, permitting a more detailed look at their solid state properties. The conductivity was measured along more than one direction in the crystal in an effort to determine whether the different spacial relationship of the molecular units in the structure might lead to anisotropic conductivity behavior. Previous work on molecular solids has shown that the activation energy for conduction is often independent of crystal direction, whereas significant differences in the conductivity may be observed.[23] Such anisotropy presumably arises from differences in the mobility of charge carriers along the various crystal directions; this, in turn, seems to be related to orbital overlaps in these directions.

In the case of $NiS_4C_4H_4$, the two activation energies which are considered experimentally reliable are quite similar, indicating that the energy required for carrier activation is independent of the crystal direction. However, the significant differences in the three conductivity values indicate that the mobility is a function of crystallographic direction in this solid. In particular, the conductivity along the [010] or needle axis direction is more than three times greater than that in either of the other directions. The $NiS_4C_4H_4$ crystal structure (shown in Figures 2, 3 and 4) reveals a stacking of planar $NiS_4C_4H_4$ molecules involving a 'head to tail' type overlap between adjacent units in the [010] direction. This is shown best in Figure 3 which is a parallel projection normal to the molecular plane, with the [101] direction coincident with a line joining the two central nickel atoms.

For $NiS_4C_4H_4$, the shortest interatomic distances between units along the [010] direction are 3.64 Å for C–S and 3.77 Å for C–C. These distances are significantly longer than separations found in most

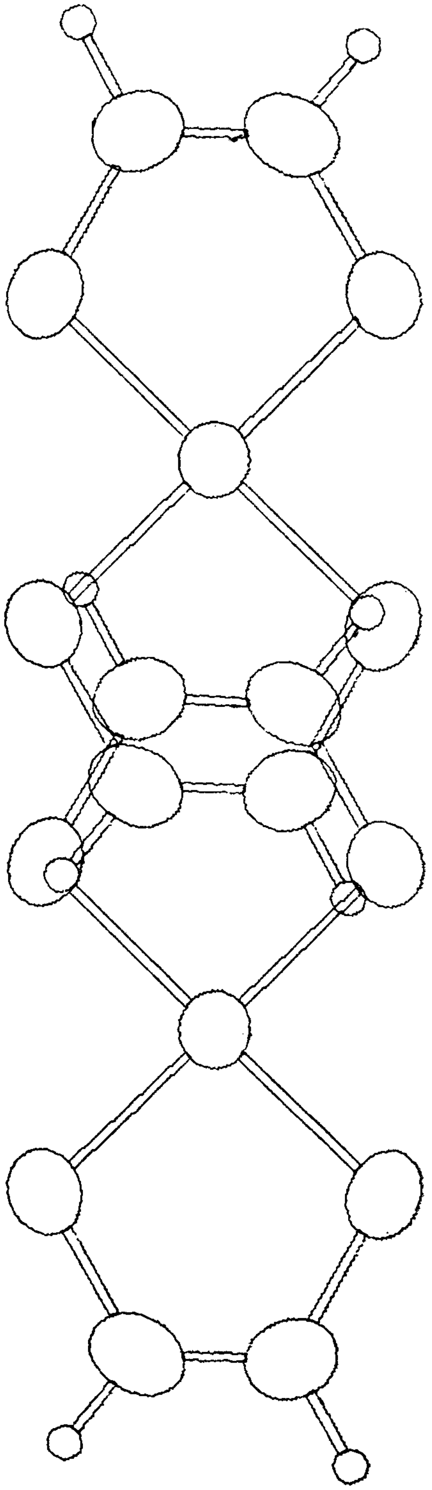

FIGURE 2 $NiS_4C_4H_4$: Projection Normal to the Molecular Plane other conductive metal complexes,[2, 3, 24] and are in the range of typical van der Waals distances for these atoms. Moreover, since the shortest intermolecular contact between a nickel atom and a non-hydrogen atom is 4.05 Å, the metal atom, at least in this case, apparently does not play a direct role in the intermolecular electron transport process. This, coupled with the observation of appreciable electrical conductivity in other aromatic sulfur-containing compounds[25] suggests that the important feature here is the presence of sulfur atoms in a chelate ring arrangement with a highly delocalized electronic structure. Intermolecular sulfur-sulfur contacts also occur along the [001] direction at 3.74 Å. However, the parallel molecular units are not overlapped in this direction and the interaction is presumably less favorable than that in the [010] direction where direct overlap of the π-molecular orbitals can occur. The only other intermolecular separations under 3.9 Å, not including hydrogen, are those involving the carbon and sulfur atoms of adjacent molecular units in the [101] direction. Although the C–C distance is 3.86 Å and the C–S distance is 3.78 Å in this direction, the angle of inclination of the molecular planes may limit the degree of intermolecular orbital overlap.

The geometric arrangement of molecular units for the $PtS_4C_4H_4$ dimer is similar to that described for the $NiS_4C_4H_4$ complex. The principal intermolecular interactions again appear to be along the needle axis, or [010] direction, where direct overlap of molecular planes can be observed in a normal projection. The conductivity results for $PtS_4C_4H_4$, shown in Table VII, are consistent with this conclusion. However, in view of the small size of the crystal and the necessity of employing a two-probe measurement technique, a detailed discussion of structure-property relationships does not seem justified in this case.

The dependence of conductivity on the metal observed for the $A^+MS_4C_4H_4^-$ complexes is contrary to that found by Rosa and Schrauzer[5] for other $MS_4C_4R_4$ (M = Ni, Pd, Pt; R = CH_3, C_6H_5, $C_6H_4OCH_3$) derivatives. Here the electrical conductivity was found to vary in direct proportion to the polarographic half-wave potential for the couple

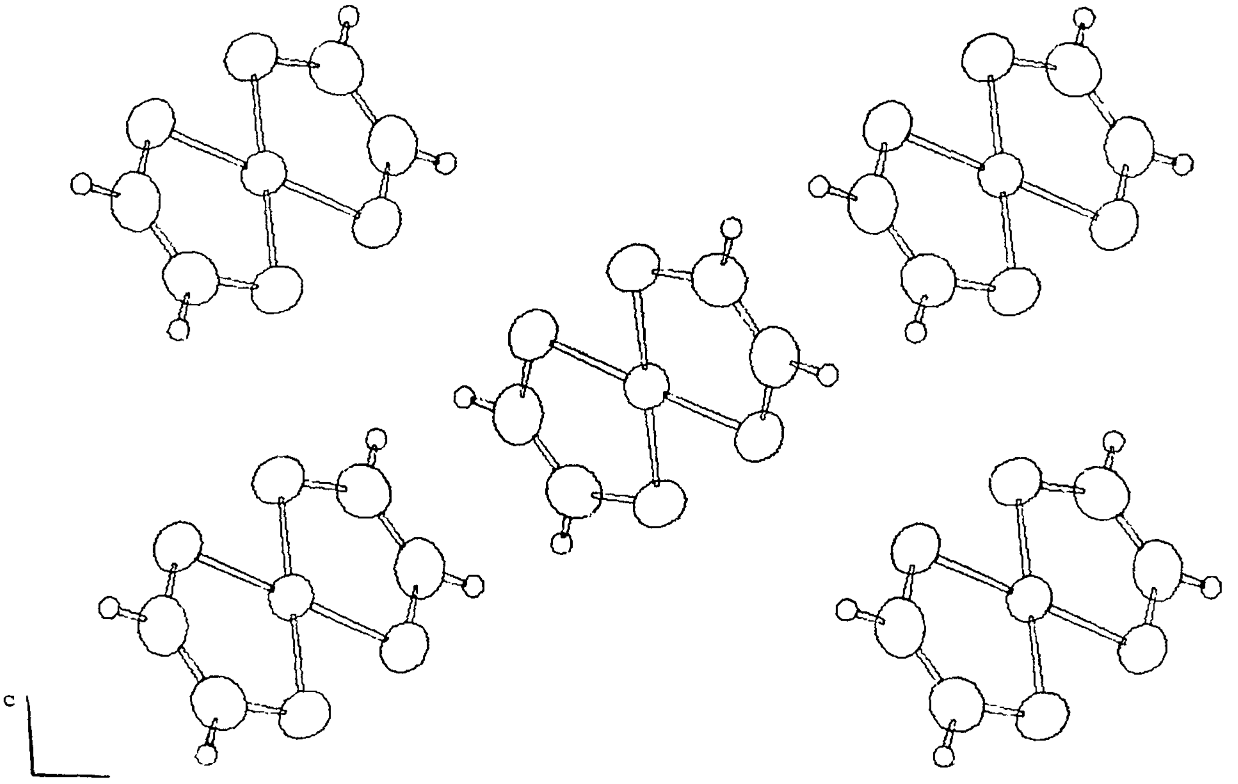

FIGURE 3 $NiS_4C_4H_4$ crystal structure; [010] projection.

$[MS_4C_4R_4] + e^- \rightleftarrows [MS_4C_4R_4]^-$ in the order Pd > Ni > Pt. This relationship between conductivity and polarographic half-wave potential was explained by presuming that electron transport in these complexes takes place in the lowest occupied π-MO and that the half-wave potentials provide a measure of the absolute energy of this orbital. As the energy of this orbital decreases (and half-wave potential increases) its electron population presumably increases, thus raising the conductivity.

Our work on the $MS_4C_4H_4{}^{n-}$ complexes indicates that this relationship may not be as generally applicable to the bis-dithiolene complexes as was supposed. In particular, the half-wave potentials for these complexes vary with the metal in the order Pd > Ni > Pt, as is the case for all of the known $MS_4C_4R_4{}^{n-}$ complexes.[4] The conductivity, on the other hand, among most of the isomorphous $A^+MS_4C_4H_4{}^-$ complexes decreases in the order Pt > Pd > Ni.

In many respects, the bis-dithiolene complexes studied herein bear a close resemblance to the organic compound tetracyanoquinodimethane (TCNQ) and its derivatives.[4] Like the bis-dithiolene complexes, TCNQ is a planar molecule with a highly delocalized electronic structure and is easily reduced to a radical anion, $TCNQ^-$.[26] The simple salts of this anion, A^+TCNQ^-, are well-known for their unusual solid state properties and exhibit room temperature conductivities as high as 2 ohm^{-1}

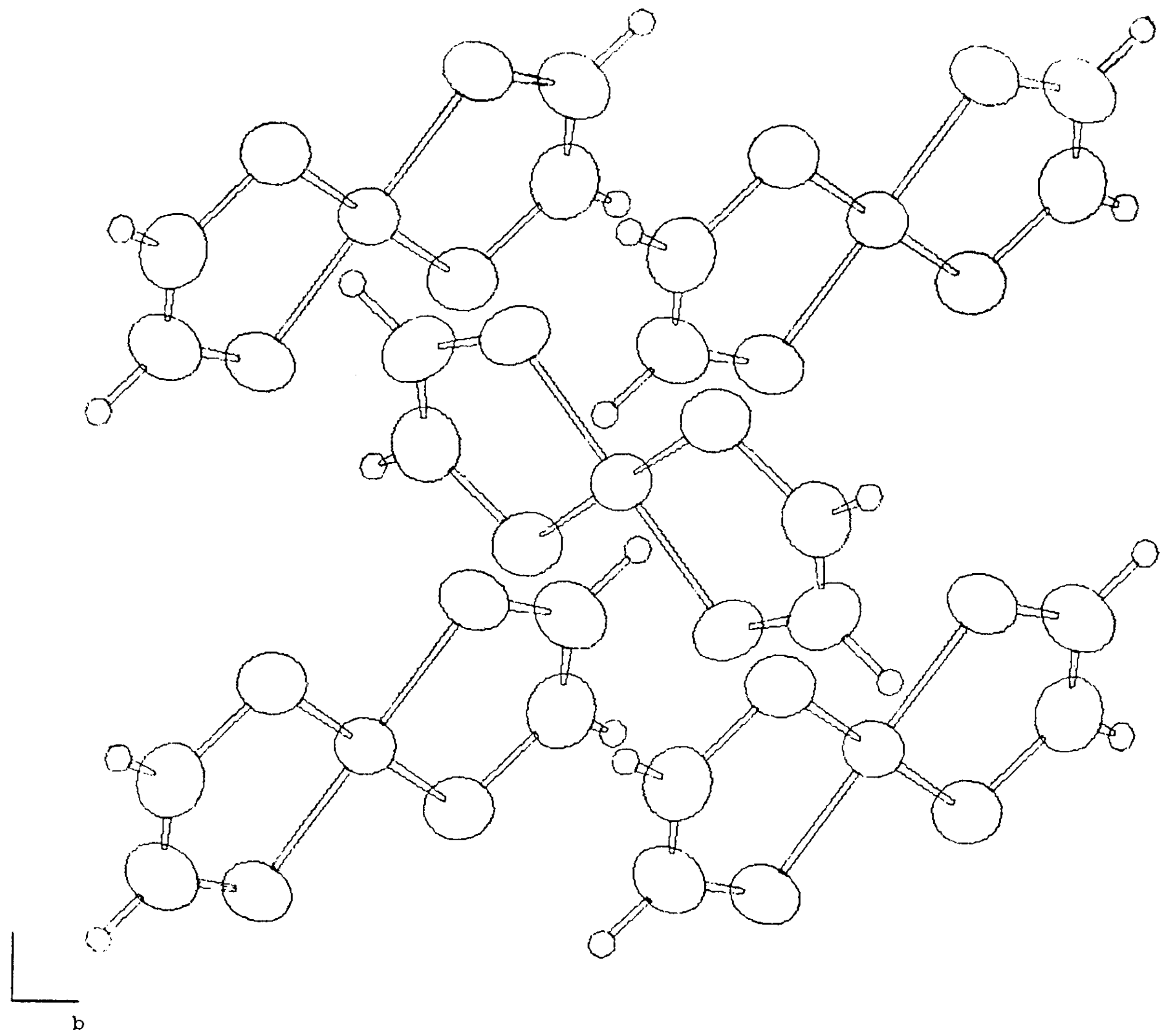

FIGURE 4 $NiS_4C_4H_4$ crystal structure; [100] projection

cm^{-1}.[27] The $TCNQ^-$ ions in many of these compounds assume a stacking arrangement[28] analogous to that found among the bis-dithiolene metal complexes resulting in extensive π-orbital overlap along the stack axis direction in the solid. As a result, the conductivity is often highly directional in character with the highest conductivity direction coincident with the stack axis. This conductivity, in most cases, is thermally activated and obeys a linear log σ vs 1/T relationship. Both the magnitude of the conductivity at room temperature and the thermal activation energy in these compounds are quite dependent upon the nature of the associated cation. This dependence of conductivity upon the cation also extends to the bis-dithiolene metal complexes where the effect is considerably larger than that produced by changes in the metal within the isomorphous $A^+MS_4C_4H_4^-$ series.

Both the polarizability of the cation and steric factors are apparently important in determining the relative magnitude of conductivity in either TCNQ or bis-dithiolene compounds. LeBlanc[29] has proposed a mechanism for conduction in TCNQ salts which predicts a reduction in the activation energy for conduction by $(1-\alpha/r^3)$, where α = the cation polarizability and r is the distance between a TCNQ molecule and the nearest cation. Indeed, the experimental results for both TCNQ salts and bis-dithiolene complexes are at least in qualitative agreement with this suggestion and it has been shown that aromatic hydrocarbons, in particular, have polarizabilities sufficient to yield a non-negligible value of α/r^3.[29]

Steric factors are obviously also of importance in determining conductivity, since a direct effect upon the crystal structure and stacking of planar TCNQ or bis-dithiolene units would be anticipated. Thus, the low steric requirements for the stacking of planar aromatic cations make them the most favorable for promoting conduction, but the addition of bulky substituent groups hinders stacking. Similarly, the R_4M^+ (M = N,P) groups are quite bulky and, in general, do not promote efficient stacking of the anion units. A recent study has demonstrated this effect for a series of TCNQ salts with tetra-n-alkyl ammonium cations.[30] In this case, the conductivity decreased monatonically with n for the $(C_nH_{2n+1})_4N^+$ series, as n was increased from zero to four. The conductivities ranged from $2 \times 10^{-5}\ \Omega^{-1}\,cm^{-1}$ to $< 10^{-11}\ \Omega^{-1}\,cm^{-1}$.

This gross similarity in the electrical properties also extends to the relationship between thermal activation energies and the conductivity among these compounds. In particular, like the bis-dithiolene complexes, there seems to be a general trend toward lower activation energies with increasing room temperature conductivity among the A^+TCNQ^- compounds. This trend is quite apparent among the A^+TCNQ^- derivatives listed in Table VI, and also includes a wide range of other compounds of this type.[31]

In view of these observations, it is apparent that this resemblance in electrical properties is more than merely fortuitous and may signal a basic similarity in the conduction mechanism for these two groups of compounds. Unfortunately, attempts to explore the analogy further by preparing mixed valence compounds of the type $A^+(MS_4C_4H_4)(MS_4C_4H_4^-)$ corresponding to the TCNQ 'complex salts' have so far been unsuccessful. Further work designed to examine the bis-dithiolene-TCNQ analogy and to prepare mixed valence bis-dithiolene complexes is currently in progress.

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