(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(14) Scattering factors for hydrogen atoms were from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(15) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972).
(16) Supplementary material.
(17) D. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(18) W. R. Busing, K. D. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program", Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(19) See for example M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).
(20) L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968).
(21) P. A. Meresse, C. Courseille, F. Leroy, and N. B. Chanh, *Acta Crystallogr., Sect. B*, **31**, 1236 (1975).
(22) For an extensive discussion on the effects of substitutents on the bond angles in substituted benzenes see A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 221 (1975).
(23) See P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 16–17 (1967), and references therein.
(24) G. Huttner and S. Lange, *Acta Crystallogr., Sect. B*, **28**, 2049 (1972).
(25) E. Keulen and F. Jellinek, *J. Organomet. Chem.*, **5** 490 (1966).
(26) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1298 (1965).
(27) L. Manajlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969).
(28) E. O. Fischer, H. P. Fritz, J. Manchat, E. Priebe, and R. Schneider, *Chem. Ber.*, **96**, 1418 (1963).
(29) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2515 (1973).
(30) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 44.
(31) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Nickel(II), Palladium(II), Platinum(II), and Platinum(IV) Complexes of the Dithiolate Ligand, $C_5H_4CS_2{}^{2-}$. Crystal Structure and Molecular Geometry of $[(C_2H_5)_4N]_2[Ni(C_5H_4CS_2)_2]$

ROBERT D. BEREMAN* and DAVID NALEWAJEK

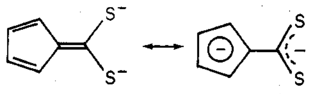
Received May 25, 1976 AIC60384B

The preparations of tetraethylammonium salts of bis(cyclopentadienedithiocarboxylato)metalate(II) where the metal is Ni, Pd, and Pt are reported as well as that of the tetraethylammonium salt of tris(cyclopentadienedithiocarboxylato)-platinate(IV). The complexes are diamagnetic. The Ni(II) complex has been examined by a single-crystal x-ray diffraction study at 3.0 ± 1.0 °C. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 6.990$ (2) Å, $b = 8.437$ (3) Å, $c = 14.475$ (6) Å, $\alpha = 96.89$ (3)°, $\beta = 90.39$ (3)°, $\gamma = 111.47$ (3)°, and $V = 787.5$ (5) Å^3. The calculated density was 1.264 g/cm^3 for a molecular weight of 599.7 with one molecule per unit cell. X-ray diffraction data (Cu Kα radiation) were collected with a Syntex $P\bar{1}$ automatic diffractometer and the structure was solved by the Patterson method. All nonhydrogen atoms other than the carbon atoms of the $(C_2H_5)_4N$ unit were refined anisotropically to convergence. Least-squares refinement resulted in final agreement factors of $R_1 = 0.091$ and $R_2 = 0.107$ for the 808 independent reflections. The molecular geometry thus determined shows the $(C_5H_4CS_2)_2Ni^{2-}$ ion to be planar, the cis S–Ni–S angles being 101.5 (1)°. The two independent Ni–S distances are 2.203 (4) and 2.198 (4) Å. The formally C–C double bonds in the C_5 ring are 1.42 (2) and 1.38 (2) Å, while the formally single bonds are 1.43 (2), 1.44 (2), and 1.50 (2) Å. The optical spectrum of the Ni(II) system is reported and interpreted in terms of this geometry. Spectroscopic data for the Pd(II), Pt(II), and Pt(IV) complexes are also reported.

Introduction

With the great deal of recent interest in metal–sulfur coordination complexes,[1-3] it is not surprising that a new dithiolate ligand type which promised to add a new dimension to the overall picture of coordination complexes has received a great deal of attention in our laboratories.[4-9] Previously, we have demonstrated that metal complexes of the $C_5H_4CS_2{}^{2-}$ moiety induce unique electronic properties at metal centers because of the specific out-of-plane π-accepting ability of ligand.

The exact extent of this π-bonding ability or rather the importance of the resonance structure Ib of the ligand when bound to a metal can be estimated from electron spin resonance studies,[3-5] the coupling constants of the ring protons,[6-8] and Mössbauer data.[7,8] In all previous cases, it has not been possible to obtain single crystals of the metal complexes for a definitive study of the nature of the carbon backbone in the five-membered ring. Recently, however, a Ni(II) complex has been isolated as small platelets which were *marginally* suitable for a single-crystal x-ray analysis. Those results as well as a spectroscopic characterization of the Ni(II), Pd(II), Pt(II), and Pt(IV) complexes are reported here.



Ia Ib

Experimental Section

Materials. Anhydrous solvents were prepared as before[4-9] except tetrahydrofuran which was distilled from Na–K amalgam. $NiBr_2$, $PdCl_2$, $PtCl_2$, and $PtCl_4$ were obtained from Research Organic/Inorganic Chemical Corp.

$Na_2C_5H_4CS_2{\cdot}C_4H_8O$. This complex was prepared as previously reported.[6]

$[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$. This complex was prepared in a manner similar to that previously reported for other transition metal complexes.[4-9] Typically, 1.07 g (4.14 × 10^{-3} mol) of $Na_2C_5H_4CS_2{\cdot}C_4H_8O$ and 0.454 g (2.07 × 10^{-3} mol) of $NiBr_2$ were added to 150 ml of CH_3CN. After stirring of this solution for 1 h at room temperature, 0.687 g (4.14 × 10^{-3} mol) of $(C_2H_5)_4NCl$ was added to the red solution. The mixture was filtered to remove NaX (X = Cl, Br). The resulting filtrate was reduced in volume several times and filtered again at each stage. A relatively small yield was obtained as red-orange platelets. Anal. Calcd for $[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$: C, 56.08; H, 8.07; N, 4.67; S, 21.39. Found: C, 55.98; H, 8.00; N, 4.68; S, 21.30.

$[(C_2H_5)_4N]_2Pd(C_5H_4CS_2)_2$. This orange-brown product ultimately crystallized as small platelets. Anal. Calcd: C, 51.95; H, 7.47; N, 4.33. Found: C, 52.03; H, 7.40; N, 4.39.

$[(C_2H_2)_4N]_2Pt(C_5H_4CS_2)_2$. Careful fractional cystallization is required during the isolation. The first few fractions of an apparently pure bright red product were considerably contaminated with NaX.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{22}	β_{12}	β_{13}	β_{23}
Ni	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.020 (1)	0.0084 (6)	0.0037 (2)	0.007 (1)	−0.0013 (9)	0.0005 (7)
S(1)	0.2943 (7)	0.0691 (6)	0.0804 (3)	0.023 (1)	0.0143 (8)	0.0046 (3)	0.009 (2)	−0.002 (1)	0.0031 (8)
S(2)	0.1054 (7)	0.0455 (6)	−0.1405 (3)	0.022 (1)	0.0119 (8)	0.0038 (2)	0.004 (2)	0.003 (1)	0.0027 (8)
N	0.213 (2)	0.562 (1)	0.2374 (8)	0.014 (3)	0.009 (2)	0.0034 (8)	0.017 (4)	−0.000 (3)	−0.000 (2)
C(1)	0.157 (3)	0.039 (2)	0.179 (1)	0.040 (5)	0.005 (2)	0.0031 (9)	0.020 (5)	−0.010 (4)	0.001 (2)
C(2)	0.225 (2)	0.069 (2)	0.271 (1)	0.017 (4)	0.006 (3)	0.0032 (9)	0.003 (5)	−0.001 (4)	−0.000 (3)
C(3)	0.448 (3)	0.118 (2)	0.301 (1)	0.027 (5)	0.009 (3)	0.0045 (11)	0.005 (6)	−0.006 (4)	0.002 (3)
C(4)	0.444 (3)	0.137 (2)	0.399 (1)	0.046 (7)	0.011 (3)	0.0049 (12)	0.009 (8)	−0.003 (5)	−0.000 (3)
C(5)	0.239 (3)	0.098 (2)	0.430 (1)	0.023 (5)	0.014 (4)	0.0052 (11)	0.007 (7)	−0.003 (4)	0.000 (3)
C(6)	0.108 (3)	0.060 (2)	0.352 (1)	0.044 (6)	0.007 (2)	0.0023 (9)	0.023 (6)	0.005 (4)	−0.000 (3)

Atom	*x*	*y*	*z*	*B*, Å^2	Atom	*x*	*y*	*z*	*B*, Å^2
C(7)	0.041 (3)	0.396 (2)	0.195 (1)	3.3 (4)	C(11)	0.307 (2)	0.682 (2)	0.163 (1)	3.1 (4)
C(8)	−0.134 (3)	0.421 (2)	0.143 (1)	4.7 (5)	C(12)	0.398 (3)	0.601 (2)	0.082 (1)	3.7 (4)
C(9)	0.134 (3)	0.665 (2)	0.314 (1)	3.6 (4)	C(13)	0.372 (3)	0.502 (2)	0.280 (1)	3.6 (4)
C(10)	0.048 (3)	0.574 (2)	0.396 (1)	4.4 (5)	C(14)	0.565 (3)	0.653 (2)	0.331 (1)	4.9 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

It was not until a brick red powder was collected that analytical purity was obtained. Anal. Calcd: C, 45.71; H, 6.57. Found: C, 45.66; H, 6.45.

$[(C_2H_5)_4N]_2Pt(C_5H_4CS_2)_3$. This complex was obtained as a bright orange microcrystalline product. Anal. Calcd: C, 46.61; H, 5.98. Found: C, 46.32; H, 6.16.

Analyses. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Spectroscopic Measurements. Infrared, optical, and NMR spectra were obtained as before.[3-9]

Crystal Preparation. Bright red-orange crystals of $[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$ were prepared by slowly cooling a saturated solution of the complex in CH_3CN. The saturated solution is a result of a typical preparation and was not prepared by redissolving the complex in CH_3CN, a procedure we found unsatisfactory.

Crystal Structure Determination

The structure of $[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$ was determined by the Molecular Structure Corporation, College Station, Tex., at 3.0 ± 1.0 °C. The complex crystallizes as thin red-orange platelets in the triclinic crystal system having one molecule per unit cell with $a = 6.990$ (2) Å, $b = 8.437$ (3) Å, $c = 14.475$ (6) Å, $\alpha = 96.89$ (3)°, $\beta = 90.39$ (3)°, $\gamma = 111.47$ (3)°, and $V = 787.5$ (5) Å^3. These cell constants and their standard deviations were determined by computer-centering of 15 reflections, followed by least-squares refinement of the setting angles. The calculated density is 1.264 g/cm^3. The choice of space group as $P1$ or $P\bar{1}$ was based on the observed C_i diffraction symmetry and no extinctions; the centrosymmetric space group $P\bar{1}$ was confirmed by successful refinement.

The crystal chosen for the intensity data collection was bounded by the (010), (0$\bar{1}$0), (101), ($\bar{1}$0$\bar{1}$), (001), and (00$\bar{1}$) faces and had approximate dimensions of 0.200 × 0.084 × 0.012 mm. The crystal was mounted in a glass capillary in a random orientation on a Syntex $P\bar{1}$ diffractometer. Cu Kα (λ 1.541 84 Å) radiation was filtered by a graphite-crystal incident-beam monochromator. A takeoff angle of 3° was used. The counter had an aperture width of 2.0 mm and was positioned 19 cm from the crystal. The average width of a reflection at half-height (from ω scans) was 0.3°. The incident-beam collimator diameter was 1.5 mm. The θ–2θ scan technique [$0 < 2\theta$ (Cu Kα) $\leq 115°$] with a variable scan rate of 4–24°/min was used. [The scan range was from 2θ (Cu Kα_1) − 1.2° to 2θ (Cu Kα_2) + 1.2°.] Stationary-crystal, stationary-counter background counts were taken at each end of the scan range. The ratio of scan time to background counting time (R) was 2.0. A total of 3077 reflections were collected of which 3002 were independent. As a check on crystal and electronic stability, three representative reflections were measured periodically and no unusual trends were observed.

For data reduction, intensities and standard deviations on intensities were calculated using the formulas $I = S(C - RB)$ and $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and p is a factor introduced to downweight intense reflections and was set to +0.07 here. Lorentz and polarization corrections were applied to the data. Neither a correction for changes in intensity of the standard reflections nor an extinction correction was necessary. An absorption correction ($\mu = 33.48$ cm^{-1}) was applied to all data; transmission factors varied from 0.687 to 0.961.

Table II. Least-Squares Planes:[a] $0.2332X - 0.9679Y - 0.0939Z + 0.1393 = 0$

Atom	*X*	*Y*	*Z*	Dist, Å
S(1)	1.8360	0.3895	1.1533	0.082
S(2)	0.6100	0.6253	−2.0166	−0.134
C(1)	0.9570	−0.0341	2.5616	0.155
C(2)	1.3327	0.0217	3.8892	0.064
C(3)	2.7329	0.3576	4.3134	0.025
C(4)	2.6385	0.3148	5.7286	−0.088
C(5)	1.3220	−0.0474	6.1763	−0.086
C(6)	0.5345	−0.1995	5.0565	−0.018
		Other Atoms		
Ni	0.0000	0.0000	0.0000	0.139

[a] *X*, *Y*, and *Z* are orthogonalized coordinates.

The structure was solved using the Patterson method. The Patterson map showed the positions of the Ni and two S atoms. Least-squares refinement of the heavy atoms resulted in agreement factors (defined below) of $R_1 = 0.35$ and $R_2 = 0.42$. The remaining nonhyrogen atoms were located in succeeding difference Fourier syntheses. All nonhydrogen atoms other than the carbon atoms of $(C_2H_5)_4N$ were refined anisotropically to convergence (isotropic thermal parameters were used for the carbon atoms of the cation). Only a few hydrogen atoms could be located in the final difference Fourier map, and, therefore, hydrogen atom contributions were not included in the refinement.

In the full-matrix least-squares refinement process, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from Cromer and Waber.[10] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[11] Only the 808 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Final-cycle least-squares refinement resulted in $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.091$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.107$. The number of observations was 808 and the number of variable parameters was 120. The standard deviation of an observation of unit weight was 1.90. The maximum shift of a parameter in the final cycle of refinement was 0.03σ.

Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $\lambda^{-1} \sin\theta$, reflection order in data collection, and various classes of indices showed no unusual trends.

The final positional and thermal parameters of all the nonhydrogen atoms are given in Table I.

Results and Discussion

The crystal structure of $[(C_2H_5)_4N]_2[Ni(C_5H_4CS_2)_2]$ consists of discrete $Ni(C_5H_4CS_2)_2^{2-}$ units and $(C_2H_5)_4N^+$ ions. No interaction between Ni atoms and nearby S atoms from other anionic units is present. The coordination about the Ni consists of a rhombically distorted planar array of S atoms. Table II displays a representation of the planarity of this system. The Ni–S bonds are not significantly different

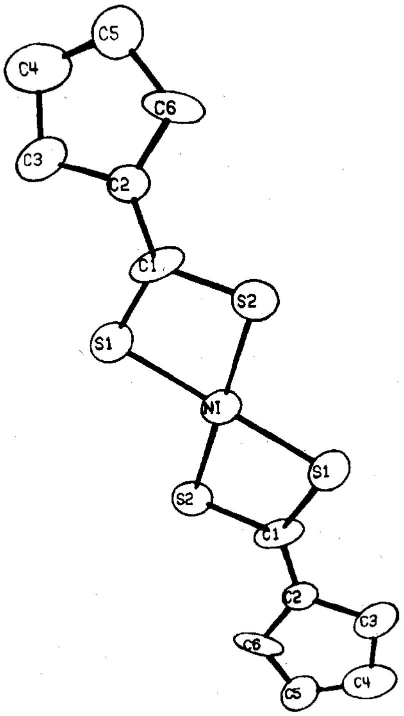


Figure 1.

for other Ni–S systems with dithiolate ligand.[3] The anion has crystallographically imposed C_i symmetry and approximate D_{2h} symmetry (Figure 1). The space lattice is such that the five-membered carbon rings of adjacent anions are parallel and are stacked one over the other (Figure 2).

Tables III and IV list all the intramolecular bond angles and distances. Of most interest are the bond distances obtained for the C–C bonds in the five-membered ring. If we assume that normal double-bond and single-bond distances are approximately 1.34 and 1.54 Å, respectively,[12] then it can be concluded that a significant amount of delocalization of electron density from the negative charge formally on the sulfur must reside on the ring itself. The formal single C–C bonds in this system average 1.45 Å and the formal double C–C bonds average 1.40 Å. It must be realized that the average values for the single- and double-bond lengths while different are within a range of 3σ. Even in an idealized $C_5H_5^-$ system, crystal lattice energies might produce asymetric bond lengths. Churchill and Kalra have shown that nonequivalence in $C_5H_5^-$ units is due to libration of the ring.[13] Nevertheless, the bond lengths here clearly seem to indicate the importance of resonance structure Ib in the bonding of the $C_5H_4CS_2^{2-}$ unit to nickel. Electron delocalization specifically must be occurring in the out-of-plane fashion. Previous studies have shown that the out-of-plane π bonding is significantly more important than in-plane π bonding.[4]

Table III. Bond Angles (deg)[a]

S(1)-Ni-S(1)	180.0 (2)	S(1)-C(1)-S(2)	106.6 (7)
S(1)-Ni-S(2)	101.5 (1)	S(1)-C(1)-C(2)	129.8 (12)
S(1)-Ni-S(2)	78.5 (1)	S(2)-C(1)-C(2)	123.6 (12)
S(1)-Ni-S(2)	78.5 (1)	C(1)-C(2)-C(3)	122.3 (14)
S(1)-Ni-S(2)	101.5 (1)	C(1)-C(2)-C(6)	128.8 (15)
S(2)-Ni-S(2)	180.0 (2)	C(3)-C(2)-C(6)	108.9 (12)
Ni-S(1)-C(1)	87.7 (5)	C(2)-C(3)-C(4)	102.3 (14)
Ni-S(2)-C(1)	86.6 (5)	C(3)-C(4)-C(5)	112.3 (14)
C(7)-N-C(9)	111.6 (9)	C(4)-C(5)-C(6)	107.5 (14)
C(7)-N-C(11)	112.1 (9)	C(2)-C(6)-C(5)	109.1 (15)
C(7)-N-C(13)	104.3 (10)	N-C(7)-C(8)	114.7 (12)
C(9)-N-C(11)	109.0 (9)	N-C(9)-C(10)	115.5 (11)
C(9)-N-C(13)	110.4 (9)	N-C(11)-C(12)	114.2 (10)
C(11)-N-C(13)	111.5 (10)	N-C(13)-C(14)	113.9 (11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Distances (Å)[a]

Ni-S(1)	2.203 (4)	C(2)-C(3)	1.501 (18)
Ni-S(2)	2.198 (4)	C(2)-C(6)	1.431 (18)
S(1)-C(1)	1.713 (15)	C(3)-C(4)	1.419 (18)
S(2)-C(1)	1.761 (15)	C(4)-C(5)	1.437 (20)
N-C(7)	1.526 (16)	C(5)-C(6)	1.377 (18)
N-C(9)	1.551 (15)	C(7)-C(8)	1.527 (18)
N-C(11)	1.546 (15)	C(9)-C(10)	1.507 (17)
N-C(13)	1.533 (15)	C(11)-C(12)	1.546 (17)
C(1)-C(2)	1.381 (16)	C(13)-C(14)	1.577 (19)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits (an additional significant figure to that used in the text is given in the table in order to more accurately present the data).

This apparent increased π-bonding capability is not reflected in the Ni–S bond distances, however. The average value of 2.20 Å here is near the average found for 1,1-dithiolate ligands of 2.21 Å.[3] This Ni–S distance, however, is significantly longer than that found for nickel–dithiolene complexes. These values unfortunately, however, do not reflect simply the difference in π-bonding ability of the ligand types but alos reflect the "bite" of the bidentate ligands. A five-membered chelate ring

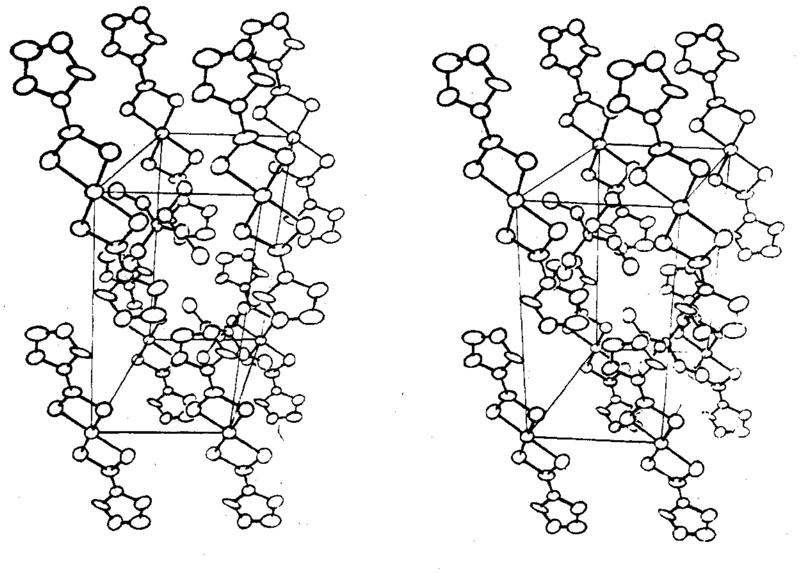


Figure 2.

Table V. Features of Electronic and Infrared Spectra (cm^{-1})[a]

	Electronic		Ir	
Complex	Freq	Assignment	Band position	Suggested origin[b]
$Na_2C_5H_4CS_2$			23 260	$n \rightarrow \pi^*$
			24 270	$n \rightarrow \sigma^*$
			30 770	$\pi \rightarrow \pi^*$
			39 220	$\pi \rightarrow \pi^*$
$[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$	385	Ni-S	18 550 s, asym	$^1A_{1g} \rightarrow {}^1A_{2g}$
	645	C-S	22 270 ms	L
			27 030 vs, asym	M → L
			35 400 ms, asym	M → L
			38 095 sh	
			40 240 w	
$[(C_2H_5)_4N]_2Pd(C_5H_4CS_2)_2$	333	Pd-S	21 280 vs, asym	$^1A_{1g} \rightarrow {}^1A_{2g}$
	642	C-S	22 830 sh	L
			24 390 sh	L
			27 397 sh	
			29 411 vs, asym	M → L
			33 557 w	
			37 520 s, asym	M → L
$[(C_2H_5)_4N]_2Pt(C_5H_4CS_2)_2$	340	Pt-S	19 380 vs, asym	$^1A_{1g} \rightarrow {}^1A_{2g}$
	641	C-S	23 530 sh	L
			29 500 vs, asym	M → L
			34 970 sh	
			36 770 w	
			41 410 s, asym	M → L
$[(C_2H_5)_4N]_2Pt(C_5H_4CS_2)_3$	339	Pt-S	19 500 vs, asym	
	645	C-S	24 090 sh	L
			29 630 vs, asym	M → L
			34 965 w	
			37 040 w	
			40 990 s, asym	M → L

[a] Obtained lubinol mulls; asym = asymetric peak without defined shoulder. [b] L indicates those peaks due to the ligand.

(including the Ni) provides an electronically more favorable environment for metal–sulfur d_π–p_π bonding interactions.

Nuclear magnetic resonance spectra of all of the complexes reported here consist of a complex set of doublets characteristic of an AA′BB′ system. Solubility did not allow a detailed interpretation as before.[7,9] The positions of the doublets were (ppm) 6.19 and 5.82 for Ni(II), 6.28 and 5.90 for Pd(II), 6.20 and 5.89 for Pt(II), and 6.18 and 5.85 for Pt(IV), all relative to TMS. The sharp features of the proton NMR spectra do clearly indicate that all of the complexes are diamagnetic.

The optical and infrared spectral features of all of the complexes discussed here are given in Table V. The ground state in each M(II) system should be $^1A_{1g}$ and the first spin-allowed transition should be $^1A_{1g} \rightarrow {}^1A_{2g}$. Unfortunately, the ligand also absorbs in the region 23 200–39 200 cm^{-1} as well. One must assume these energy transitions in the ligand change upon complexation since we know the electronic structure as evidenced by NMR differences is affected.[7,9] The similarity in the NMR data for these complexes does, however, indicate that any optical transitions due to the ligand alone should remain approximately constant through the series. The only bands which might be confidently assigned are the lowest energy bands in the spectra of the Ni(II), Pd(II), and Pt(II) complexes. The other *suggested assignments* are presented in Table V.

The energies of the single sharp M–S infrared peaks are so close for the PtS_6, PtS_4, and PdS_4 chromophores as opposed to the NiS_4 chromophore that it is entirely possible that, within the former series, the coordination geometry is different from that of the NiS_4 system. Possibly a MS_6 environment might exist in all three cases. Dimer or polymeric behavior has been suggested for both the iron(II) and tin(II) complexes of this ligand.[8,9] There is certainly no reason to assume these complexes are isostructural with the Ni(II) complex.

Acknowledgment. We thank Professor M. R. Churchill for his help in the preparation of this article. R.D.B. gratefully acknowledges support from a Camille and Henry Deyfus Foundation fellowship.

Registry No. $Na_2C_5H_4CS_2$, 3357-50-4; $[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$, 60525-69-1; $[(C_2H_5)_4N]_2Pd(C_5H_4CS_2)_2$, 60525-71-5; $[(C_2H_5)_4N]_2Pt(C_5H_4CS_2)_2$, 60525-73-7; $[(C_2H_5)_4N]_2Pt(C_5H_4CS_2)_3$, 60525-75-9.

Supplementary Material Available: Listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. A. MeCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(2) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 294 (1970).
(3) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
(4) P. C. Savino and R D. Bereman, *Inorg. Chem.*, **12**, 173 (1973).
(5) B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, **12**, 2997 (1973).
(6) B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, **14**, 1417 (1975).
(7) B. J. Kalbacher and R. D. Bereman, *J. Inorg. Nucl. Chem.*, **38**, 471 (1976).
(8) R. D. Bereman, M. L. Good, B. J. Kalbacher, and J. Buttone, *Inorg. Chem.*, **15**, 618 (1976).
(9) R. D. Bereman, M. L. Good, P. S. Savino, and J. Buttone, submitted for publication.
(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(12) *Chem. Soc., Spec. Publ.*, **No. 18**, S14s–S16s (1965).
(13) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).