Inorganica Chimica Acta, 63 (1982) 75–83

A Systematic Study of Steric Control of the Thiocyanate's Bonding Mode in [Pd(substituted diamine)(thiocyanate)$_2$] and [Pd(substituted diamine)$_2$](SCN)$_2$ Complexes

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Received March 17, 1982

Steric control of the thiocyanate's bonding mode in Pd(II) complexes has been systematically studied by the synthesis and characterization (elemental analysis, IR (solid state and solution), molar conductance, ^{13}C NMR and electronic spectral measurements) of 14 complexes containing bidentate substituted diamines representing a wide range of steric requirements. In the solid state, the diamines producing the least steric hindrance (1,2-diamino-2-methylpropane, 1,2-bis(methylamino)ethane, 1-amino-2-dimethylaminoethane, 2-aminomethylpyridine) were found to form ionic complexes of the type [Pd(diamine)$_2$](SCN)$_2$. Diamines having intermediate steric demands (1,2-bis(dimethylamino)ethane, 1,2-bis(phenylamino)ethane, 1-amino-2-morpholinoethane, 1-amino-2-pyrrolidinoethane, 1-amino-2-piperidinoethane) produced S-bound [Pd(diamine)(SCN)$_2$] complexes, whereas those exhibiting the greatest steric requirements (1,2-dipiperidinoethane, 1,2-dipyrrolidinoethane, 1,3-bis(dimethylamino)propane) yielded N-bound [Pd(diamine)(NCS)$_2$] complexes. Two diamines did not follow these trends: the sterically undemanding 1,2-diaminobenzene produced a neutral S-bound complex, as did the bulky 1,2-dimorpholinoethane. The structure of the 1,2-diamino-2-methylpropane complex was confirmed by the results of a single crystal X-ray structure determination [$PdS_2N_6C_{10}H_{24}$: a = 6.834(2), b = 10.304(2), c = 11.704(2) Å, β = 91.59(2)°, $P2_1/c$, Z = 2], as was the structure of the [Pd(1-amino-2-pyrrolidinoethane)$_2$](SCN)$_2$ complex resulting from the attempted recrystallization of [Pd(1-amino-2-pyrrolidinoethane)(SCN)$_2$] in hot DMF [$PdS_2N_6C_{14}H_{28}$; a = 6.805(9), b = 16.765(31), c = 8.964(10) Å, β = 111.22(9)°, $P2_1/c$, Z = 2]. In DMF solution, all of the neutral S-bound complexes were found to undergo partial or full linkage isomerization to the N-bound forms, with the exception of those containing 1,2-bis(phenylamino)ethane and 1,2-diaminobenzene.

Introduction

Although the existence of steric control of the thiocyanate's bonding mode was first discovered eighteen years ago [1] ([Pd(diethylenetriamine)SCN]$^+$ *versus* [Pd(1,1,7,7-tetraethyldiethylenetriamine)NCS]$^+$], virtually all of the subsequent work involving this aspect of the coordination chemistry of the thiocyanate ion has focused on the effects of ligands other than amines [2, 3]. Most recent work [4–11] has involved ligands containing Group VA and VIA donor atoms in the third and

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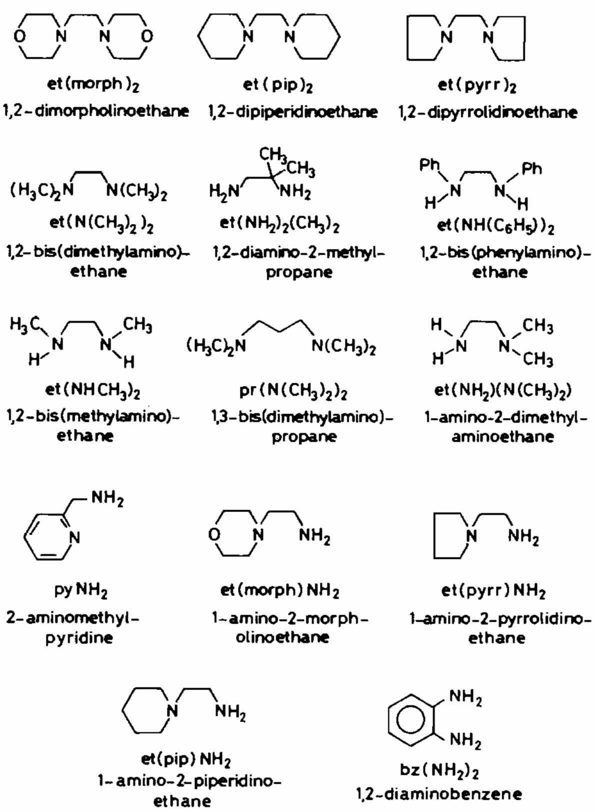

Fig. 1. Structures, abbreviations and names of the diamines employed in this study.

later rows of the periodic table, with an emphasis on mono- and bidentate phosphines [4–10].

In view of the controversy which has surrounded the interpretation of the results of these studies [2–11] in terms of competing steric and electronic effects, a systematic investigation of the effects of varied steric hindrance in palladium(II)–thiocyanate complexes containing non-π-bonding amines appeared to us to be highly desirable. Accordingly, we now wish to report the results of our study involving complexes of the type [Pd(substituted diamine)(thiocyanate)$_2$], where substituted diamine represents one of the diamines whose structures, abbreviations and names are shown in Fig. 1.

Experimental

Preparation of Ligands

Most of these compounds are commercially available and were used as received from the manufacturer without further purification. The compounds 1,2-dipyrrolidino-, 1,2-dipiperidino- and 1,2-dimorpholinoethane were synthesized by literature methods [12, 13].

Preparation of Complexes

All of the complexes, except for those of 1,2-bis-(dimethylamino)ethane and -propane and 1,2-bis-(phenylamino)ethane were prepared by the same method, exemplified in detail as follows for the 1,2-bis(methylamino)ethane complex: To 1.0 g (5.6 mmol) of $PdCl_2$ dissolved in 25 ml DMF was added 2.3 g (24 mmol) of KSCN, also in 25 ml DMF. The resulting deep red solution was stirred with gentle warming for 1 hr, after which time it was filtered to remove the KCl byproduct. To the filtrate was added 0.50 g (5.6 mmol) of 1,2-bis(methylamino)ethane, with stirring. The solution was then reduced to dryness on a rotary evaporator, and 10 ml of methanol was added to the remaining material. In most cases, the complex precipitated after a time; however, in one or two cases distilled water was added dropwise until the solution became turbid, and the product precipitated shortly thereafter. The complex was isolated by filtration, washed with a minimum of cold methanol and then with diethyl ether, and finally vacuum dried. The yield was 0.78 g (45%). Both the $[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$ and the $[Pd(et(pyrr)NH_2)(SCN)_2]$ complexes were prepared in this manner, and the chemical analyses, conductance and spectral measurements reported herein were made on these samples. In order to grow suitable crystals for X-ray structure determinations, these two complexes were dissolved in DMF, a small volume of alcohol/water was added, and the mixtures were heated to ~80 °C on top of a drying oven over a two-week period. The X-ray structure determination of the latter complex (*vide infra*) revealed that the recrystallization procedure had resulted in its being converted into the ionic complex $[Pd(et(pyrr)NH_2)_2](SCN)_2$.

Dithiocyanato(1,2-bis(dimethylamino)ethane)palladium(II), $[Pd(et(NMe_2)_2(NCS)_2]$, was prepared by a procedure similar to that described by Hassel [14]. Potassium tetrathiocyanatopalladate(II) (1.85 g, 4.42 mmol) was dissolved in 100 ml of a 50% by volume ethanol–water mixture. The ligand (0.60 ml, 4.8 mmol) was added neat to the metal containing solution. After the resulting mixture was stirred for about five min, a yellow solid precipitated. The yield was increased by reducing the volume of the solution by aspiration. The product was isolated by filtration, and washed with water, a small amount of ethanol, and diethyl ether. Yield, 91%.

Diisothiocyanato-1,3-bis(dimethylamino)propanepalladium(II), $[Pd(pr(NMe_2)_2(NCS)_2]$, was prepared by the following method, after several unsuccessful attempts by the method of Hassel [14]. Potassium tetrathiocyanatopalladate(II) (2.36 g, 5.67 mmol) was dissolved in approximately 60 ml of acetone at room temperature. To this solution was added an excess of neat ligand (8.24 g, 63.3 mmol). The resulting red solution was stirred for about two min, where-

TABLE I. Melting Points and Elemental Analyses for the [Pd(substituted diamine)(thiocyanate)$_2$] Complexes.

Diamine	m.p. (°C)	Color	%C found	%H found	%C calc	%H calc
et(morph)$_2$	177	yellow	34.39	4.49	34.12	4.77
et(pip)$_2$	157	burnt orange	39.82	5.23	40.18	5.78
et(pyrr)$_2$	159	yellow	36.33	4.47	36.91	5.16
et(N(CH$_3$)$_2$)$_2$[a]	199	yellow	28.31	4.75	28.39	4.77
et(NH$_2$)$_2$(CH$_3$)$_2$[b]	238	yellow	30.31	5.77	30.13	6.02
et(NH(C$_6$H$_5$))$_2$[c]	169	orange	43.92	3.75	44.19	3.71
et(NHCH$_3$)$_2$[b]	167	reddish yellow	30.29	5.84	30.13	6.02
pr(N(CH$_3$)$_2$)$_2$	121	gold	30.70	4.99	30.64	5.14
et(NH$_2$)(N(CH$_3$)$_2$)[b]	172	pale yellow	30.04	5.70	30.13	6.02
pyNH$_2$[b]	197	pale brown	38.18	3.06	38.33	3.65
et(morph)NH$_2$	186	gold	27.30	3.87	27.25	4.00
et(pyrr)NH$_2$	180	gold	28.33	3.76	28.54	4.19
et(pip)NH$_2$	171	yellow	30.42	4.42	30.82	4.60
bz(NH$_2$)$_2$	180	brown	28.89	2.11	29.06	2.44

[a] %N calc 16.54, %S calc 18.93; %N found 16.49, %S found 18.94. [b] Ionic, calculated percentages are for [Pd(diamine)$_2$]-(SCN)$_2$. [c] %N calc 12.88, %S calc 14.75; %N found 12.83, %S found 14.99.

upon the volume was reduced by aspiration until a solid began to precipitate. A mixture of 100 ml of water and 150 ml of diethyl ether was then added and the resulting slurry was stirred for approximately fifteen min. Filtration of the bilayered solution yielded a gold colored solid. The solid was washed with small portions of water and diethyl ether, and dried over Drierite under vacuum. Yield, 78%.

Dithiocyanato(1,2-bis(phenylamino)ethane)palladium(II), [Pd(et(NH(C$_6$H$_5$))$_2$(SCN)$_2$], was prepared in a manner similar to that reported by Hassel [14]. Potassium tetrathiocyanatopalladate(II) (0.959 g, 2.29 mmol) was dissolved in 60 ml of a 50/50 water–ethanol mixture. The ligand (0.537 g, 2.53 mmol), dissolved in 40 ml of ethanol, was then added dropwise to the metal containing solution at room temperature. The red solution immediately turned orange which the concurrent formation of an orange solid. The solid was isolated by filtration and washed successively with small portions of water, ethanol, and diethyl ether. Yield, 93%.

The melting points and elemental analyses of the complexes are shown in Table I.

Physical Measurements

Infrared spectra of the complexes were recorded on Perkin-Elmer 180 and 599 spectrophotometers, using a 10X abscissa scale expansion in the ν_{CN} range (2300–2000 cm^{-1}). The IR spectra of solid samples were obtained using Nujol mulls spread between KBr or NaCl plates. Matched 1.1 mm CaF$_2$ cells were utilized for the solution measurements. Integrated absorption intensities of the thiocyanate ν_{CN} bands were determined by Ramsay's method of direct integration [15]. A new internal standard, 1,4-dicyanobenzene, has been evaluated [16] for use in infrared ν_{CN} intensity methods for the determination of the thiocyanate's bonding mode. The diamine–thiocyanate palladium(II) complexes were studied utilizing this standard. Additional spectra were obtained with a salicylic acid internal standard [17] for comparison.

Electronic spectra of the complexes were recorded at room temperature on a Cary 14 spectrophotometer, using DMF solutions in 1 cm quartz cells. Conductivity studies on the complexes were performed at 25 ± 0.1 °C. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made using a Yellow Springs Instruments conductivity cell, model 3403, and were measured with an Industrial Instruments conductivity bridge, model RC16B2, which was adapted in-house for use with a Tektronix type 310 oscilloscope. Molar conductances were calculated from the equation below, where K, the cell constant,

$$\lambda_m = \frac{1000K}{R[C]}$$

has been determined to be 1.0016 from measurements performed on standard KCl solutions [18]. R is the volume-corrected resistance, and [C] is the molar concentration of the species studied. Conduc-

TABLE II. Crystal Data.

	$[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$(I)	$[Pd(et(pyrr)NH_2)_2](SCN)_2$(II)
Formula	$PdS_2N_6C_{10}H_{24}$	$PdS_2N_6C_{14}H_{28}$
Formula Weight	399.2	451.2
Space group	$P2_1/c$	$P2_1/c$
Systematic absences 0k0	k = 2n + 1	k = 2n + 1
Systematic absences n0l	l = 2n + 1	l = 2n + 1
a	6.834(2) A	6.805(9) A
b	10.304(2) A	16.765(31) A
c	11.704(2) A	8.964(10) A
β	91.59(2)°	111.22(9)°
V	823.83 A^3	953.35 A^3
Z	2	2
F(000)	408	464
$Density_c$	1.608 g cm^{-3}	1.571 g cm^{-3}
$\mu(MoK_\alpha)$	14.71 cm^{-1}	12.95 cm^{-1}
Transmission factors	0.8905–0.9146	

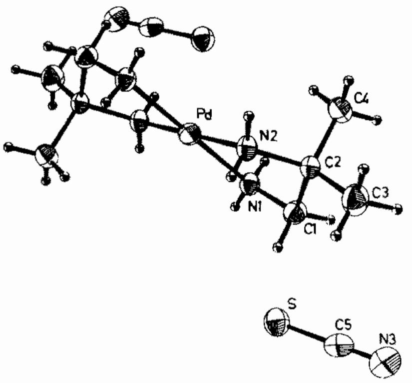

Fig. 2. Projection view of bis(1,2-diamino-2-methylpropane)-palladium(II) thiocyanate, $[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$ (structure I) with atom numbering scheme.

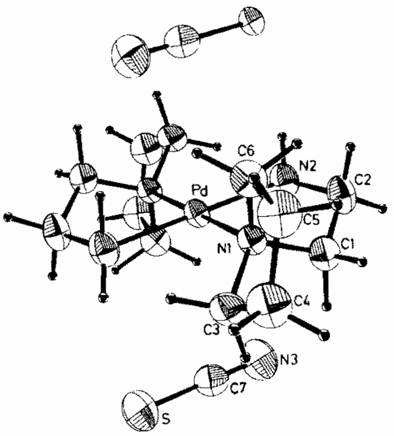

Fig. 3. Projection view of bis(1-amino-2-pyrrolidinoethane)-palladium(II) thiocyanate, $[Pd(et(pyrr)NH_2)_2](SCN)_2$ (structure II), with atom numbering scheme.

tance ranges for electrolytes were taken from published values [19].

The $^{13}C\{^1H\}$ NMR spectra of the complexes were recorded at 25.00 MHz on a JEOL FX-100 Fourier transform nuclear magnetic resonance spectrometer, equipped with a JEOL 980B computer. All line transitions for FT mode spectra were automatically determined using the JEOL FAFT 08/11 software accessory to the computer. The spectrometer was fitted with the NM-3980 multinuclear observation system utilizing a General Radio GR 1061 frequency synthesizer. The probe, which accommodated 10 mm diameter tubes, was equipped with a JES-VT-3 variable temperature controller. All $^{13}C\{^1H\}$ chemical shifts were recorded relative to DMF and corrected to tetramethylsilane (TMS). The spectrometer was operated in a ^7Li lock mode (external) at 38.70484 MHz. Samples were prepared by dissolving the complex in DMF and then filtering the solution through a disposable pipette, which had a portion of a Kimwipe inserted into it, into a 10 mm NMR tube. This filtering process was to remove any insoluble material which could adversely affect the magnetic homogeneity of the sample in the field.

Melting points of the various complexes were obtained on a Hoover melting point apparatus, and are uncorrected. Microanalyses were carried out by

TABLE III. Positional Parameters.

$[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$ (I)

Atom	x(σ(x))	y(σ(y))	z(σ(z))
Pd	0.0000	0.5000	0.5000
S	0.5770(1)	0.4477(1)	0.1940(1)
N1	0.2427(3)	0.4212(2)	0.4290(2)
N2	−0.1376(3)	0.3455(2)	0.4254(2)
N3	0.5358(4)	0.2025(3)	0.0927(3)
C1	0.1832(4)	0.3128(3)	0.3520(2)
C2	0.0101(4)	0.2419(3)	0.4009(2)
C3	−0.0744(5)	0.1446(3)	0.3149(3)
C4	0.0676(5)	0.1753(3)	0.5135(3)
C5	0.5524(4)	0.3041(4)	0.1341(3)
H1	0.313(5)	0.474(3)	0.399(3)
H2	0.320(5)	0.397(3)	0.486(3)
H3	−0.196(5)	0.370(3)	0.365(3)
H4	−0.234(5)	0.317(3)	0.463(3)
H11	0.287(5)	0.254(3)	0.349(3)
H12	0.142(5)	0.350(3)	0.281(3)
H31	0.013(5)	0.076(3)	0.303(3)
H32	−0.184	0.107(3)	0.347(3)
H33	−0.110(5)	0.185(4)	0.251(3)
H41	0.112(5)	0.235(3)	0.571(3)
H42	−0.044(5)	0.136(3)	0.541(3)
H43	0.162(5)	0.113(3)	0.503(3)

$[Pd(et(pyrr)NH_2)_2](SCN)_2$ (II)

Atom	x(σ(x))	y(σ(y))	z(σ(z))
Pd	0.0000	0.5000	0.5000
S1	−0.0162(2)	0.6424(1)	0.1295(2)
C7	0.1826(8)	0.5819(3)	0.2156(6)
N3	0.3204(7)	0.5394(3)	0.2761(6)
N1	0.8677(5)	0.4113(2)	0.3320(4)
N2	0.2286(6)	0.4167(2)	0.6018(5)
C1	0.0521(7)	0.3633(3)	0.3305(6)
C2	0.1928(8)	0.3441(3)	0.4998(6)
C3	0.7404(8)	0.4362(3)	0.1621(5)
C4	0.6134(9)	0.3623(4)	0.0862(6)
C5	0.5841(8)	0.3165(3)	0.2244(6)
C6	0.7111(8)	0.3632(3)	0.3761(6)
HN1	0.2864	0.4436	0.5187
HN2	0.2439	0.4045	0.7092
H11	0.1456	0.3969	0.2638
H12	0.0154	0.3171	0.2687
H21	0.1219	0.3033	0.5564
H22	0.3342	0.3215	0.4995
H31	0.8469	0.4541	0.1053
H32	0.6352	0.4774	0.1782
H41	0.6779	0.3256	0.0268
H42	0.4797	0.3789	0.0130
H51	0.6141	0.2595	0.2123
H52	0.4521	0.3072	0.2408
H61	0.6193	0.3965	0.4235
H62	0.7906	0.3106	0.4424

TABLE IV. Bond Distances (Å) and Angles (°)

$[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$ (I)

Pd–N1	2.044(2)
Pd–N2	2.033(2)
N1–C1	1.486(4)
C1–C2	1.516(4)
C2–C3	1.523(5)
C2–C4	1.528(4)
C2–N2	1.502(4)
S–C5	1.644(4)
C5–N3	1.158(5)
N1–H1	0.81(3)
N1–H2	0.87(3)
N2–H3	0.84(3)
N2–H4	0.86(3)
C1–H11	0.94(3)
C1–H12	0.95(3)
C3–H31	0.94(3)
C3–H32	0.93(4)
C3–H33	0.88(4)
C4–H41	0.95(3)
C4–H42	0.92(3)
C4–H43	0.92(3)
N1–Pd–N2	83.4(1)
N2′–Pd–N1	96.6(1)
Pd–N1–C1	109.5(2)
N1–C1–C2	109.7(2)
C1–C2–N2	105.4(2)
C1–C2–C3	110.7(2)
C1–C2–C4	110.9(2)
N2–C2–C3	110.5(2)
N2–C2–C4	108.2(2)
C3–C2–C4	111.0(2)
Pd–N2–C2	109.5(2)
S–C5–N3	179.4(3)

$[Pd(et(pyrr)NH_2)_2](SCN)_2$ (II)

Pd–N1	2.082(3)	N1–Pd–N2	83.6(1)
Pd–N2	2.049(4)	N1–Pd–N2′	96.3(1)
N1–C1	1.498(7)	Pd–N1–C1	104.4(2)
N1–C3	1.515(5)	Pd–N1–C3	118.0(3)
N1–C6	1.504(7)	Pd–N1–C6	111.0(3)
N2–C2	1.495(7)	Pd–N2–C2	111.1(2)
C1–C2	1.509(6)	C1–N1–C3	108.4(4)
C3–C4	1.529(8)	C1–N1–C6	112.9(4)
C4–C5	1.536(9)	C3–N1–C6	102.3(3)
C5–C6	1.538(7)	N1–C1–C2	109.5(4)
		N2–C2–C1	110.1(4)
S1–C7	1.646(5)	N1–C3–C4	104.3(4)
C7–N3	1.149(7)	C3–C4–C5	105.5(4)
		C4–C5–C6	105.2(4)
		C5–C6–N1	105.4(4)
		S1–C7–N3	179.6(16)

TABLE V. Infrared Data for the [Pd(substituted diamine)(CNS)$_2$] and [Pd(substituted diamine)$_2$](SCN)$_2$ Complexes.

Diamine	ν_{CN}[a], cm^{-1} (Nujol mull)	ISR[b]		DMF soln		CH$_3$OH soln[i]		Acetone soln		CH$_2$Cl$_2$ soln[m]	
		DCB[c]	SA[d]	ν_{CN}[a], cm^{-1}	A[e]	ν_{CN}[a], cm^{-1}	A[e]	ν_{CN}[a], cm^{-1}	A[e]	ν_{CN}[a], cm^{-1}	A[e]
et(morph)$_2$	2129s, 2123s (S) 2079w 2056vw	17.9	1.96	2106s,br(N)	8.3	[j]	[j]	[j]	[j]	[j]	[j]
et(pip)$_2$	2123s, sp(S) 2100s, br(N) 2056sh	15.1	1.60	2105s,br(N)	8.5	2120s, br(S)	2.1	2101s, br(N)	11	2121sh 2102(N) 2054sh	6.9
et(pyrr)$_2$	2106s, 2088s, br (N)	17.6	3.34	2106s, br(N)	9.6	2098s, br(N)	[k]	2098s, br(N)	4.2	2104(N)	5.3
et(N(CH$_3$)$_2$)$_2$	2121s, br(S)	14.9	2.00	2106s, br(N) 2061w	9.7	2122s, br(S)	2.6	2100s, br(N)	7.4	2113(S) 2102(N)	[g]
et(NH$_2$)$_2$(CH$_3$)$_2$	2110 vw 2040 vs, br(ionic)	13.5	0.70	2060s, br(ionic)	5.4[f]	2088w, br(N)	[i]	2119vw 2062m (ionic)	[k]	2050(ionic)	[k]
et(NH(C$_6$H$_5$))$_2$	2112s, br(S)	8.7	0.64	2119s, sp(S) 2046vw	2.1	2125s (S)	4.3	2120 (S)	[h]	2112 (S)	[k]
et(NHCH$_3$)$_2$	2067s, br(ionic) 2041vw 2021w	6.0	0.28	2061s, br(ionic)	5.6[f]	[i]	[i]	2115 br(S)	4.0	2120vw 2060w(ionic)	[k]
pr(N(CH$_3$)$_2$)$_2$	2113sh 2093s, br(N)	67.0	3.23	2109s, br(N) 2050vw	5.5	[j]	[j]	2150 (bridging) 2120(S)	[h]	2098vw(N)	[k]
et(NH$_2$)(N(CH$_3$)$_2$)	2060s, br(ionic) 2036w 2015w	7.6	0.75	2060s (ionic)	5.1[f]	[i]	[i]	[l]	[g]	2050vw(ionic)	[k]
pyNH$_2$	2061s, br(ionic) 2034vw 2013vw	8.1	0.31	2119w 2101w 2060s, br(ionic)	4.2[f]	2126s, sp(S) 2091s, br(N)	[g]	2119vw 2098s(N) 2062w	[k]	2050vw(ionic)	[k]
et(morph)NH$_2$	2122s, sp(S) 2084w	8.5	0.59	2118s, sp(S) 2103s, br(N)	[g]	2121s, sp(S) 2102sh	0.99	2119s(S) 2101s(N)	[g]	2025vw (ionic)	[k]
et(pyrr)NH$_2$	2122s, sp(S) 2085vw	5.3	0.68	2105s, br 2098s, br (?)	[h]	2122s, sp(S)	3.4	2118s(S) 2108s(N)	[g]	2115w(S)	[k]
et(pip)NH$_2$	2123s, sp(S) 2097sh 2076w	5.7	0.77	2114s(S) 2103s(N)	[g]	2120m (S)	[k]	2166m(bridging) 2155sh 2116s(S) 2099s(N)	[g]	[j]	[j]
bz(NH$_2$)$_2$	2129vw	7.2	1.03	2120s, br(S)	3.9	2124s(S)	[k]	2167s,br (bridging)	[g]	2110vw(S)	[k]
	2116s(S) 2088vw 2067vw					2102sh		2122s, sp(S)			

[a] Bonding mode of predominant isomer(s) shown in parentheses. Abbreviations: s, strong; m, medium; w, weak; sp, sharp; br, broad, sh, shoulder. [b] Internal standard ratio. [c] 1,4-dicyanobenzene internal standard (ref. 17). [d] Salicylic acid internal standard (ref. 18). [e] Integrated absorption intensity (M^{-1} cm^{-2}) × 10^{-4}. [f] Calculated assuming complex to be [Pd(diamine)$_2$](SCN)$_2$. [g] A not calculable, since concentrations of isomers not known. [h] Not determined. [i] Solvent interference below 2080 cm^{-1}. [j] Insufficient solubility. [k] Saturated solution, concentration unknown. [l] Probably undergoes linkage isomerism upon dissolution; orange solution turns yellow, concomitant with a diminution in intensity of a ν_{CN} band at 2117 cm^{-1} (m(S)) and the growth of a ν_{CN} band at 2103 cm^{-1} (m, br(N)). [m] Very poor solubility.

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Single crystal X-ray data for bis(1,2-diamino-2-methylpropane)palladium(II) thiocyanate, $[Pd(et(NH_2)_2(CH_3)_2)_2](SCN)_2$ ($PdS_2N_6C_{10}H_{24}$, structure I) and bis(1-amino-2-pyrrolidinoethane)palladium(II) thiocyanate, $[Pd(et(pyrr)NH_2)_2](SCN)_2$ ($PdS_2N_6C_{14}H_{28}$, structure II) were collected using automated diffraction equipment at room temperature (MoK_α; $\lambda = 0.71069$ Å using a $\theta - 2\theta$ scan mode). Cell dimensions and space groups were determined during normal alignment procedures (Table II). The observed data ($I > 3\sigma(I)$) were corrected for background, Lorentz and polarization effects. The structures were solved using heavy atom techniques and refinement of scale factor, positional and anisotropic thermal parameters (hydrogen positions, but not thermal parameters, were refined for structure II; for I, hydrogen positions were included but not refined) reached R = 3.6% for I and R = 2.4% for II, where $R = (\Sigma \| F_o| - |F_c\| / \Sigma |F_o|) \times 100$. Unit weights were used throughout. Projection views (I, Fig. 2; II, Fig. 3) are based upon the determined positional and thermal parameters*. Positional parameters and calculated bond angles and distances appear in Tables III and IV.

Results and Discussion

Infrared spectral data for the complexes, both in the solid state (as Nujol mulls) and in various solutions, are shown in Table V. It is probable that the thiocyanate bonding modes observed in the solid state represent kinetically trapped products in a number of cases. This is due to the method of preparation, wherein N-bonding for the thiocyanates can only occur as a consequence of linkage isomerism subsequent to coordination of the diamine. Secondly, the products were isolated from H-bonding solvents which tend [20] to stabilize the S-bonded isomer.

Nonetheless, effects due to the varying steric hindrance created by the diamines are still evident. The complexes initially isolated as ionic $[Pd(diamine)_2](SCN)_2$ species involve diamines [$et(NH_2)_2(CH_3)_2$, $et(NHCH_3)_2$, $et(NH_2)(N(CH_3)_2)$, $pyNH_2$] which, as a group, exhibit less steric hindrance. Likewise, the few complexes which exhibit N-bonding in the solid state involve diamines [$et(pip)_2$, $et(pyrr)_2$ $pr(N(CH_3)_2)_2$] which create the greatest steric hindrance. Evidence for the concurrent influence of kinetic factors is found in the unrealized expectations that the $bz(NH_2)_2$ complex should be found in the ionic group, and the $et(morph)_2$ complex should be found in the N-bound group.

For the most part, the ISR values tend to reflect the indicated bonding modes quite nicely. ISR values greater than 20 (using 1,4-dicyanobenzene as the internal standard [16]) or greater than 1.5 (using salicylic acid as the internal standard [17]) are indicative of N-bound thiocyanates. However, it has previously been noted [16] that *cis*-square planar complexes of the type $[PdL_2(thiocyanate)_2]$ sometimes exhibit inflated ISR values due to slightly non-degenerate, but unresolvable, in-phase and out-of-phase ν_{CN} stretching bands which artificially enhance the half-band width. The $et(N(CH_3)_2)_2$ complex is an excellent example of this effect, since it has independently been shown [21], using ^{14}N NQR measurements, to be S-bound in the solid state. The $et(morph)_2$ complex behaves in a similar manner.

Structures I (Fig. 2) and II (Fig. 3) show palladium on a center of symmetry and bound to the nitrogens of two substituted ethylenediamine ligands (Pd–N distances 2.033(2)–2.082(3) Å) in square planar configuration (N1–Pd–N2 angles 83.4(1) and 83.6(1)°; N1–Pd–N2′ angles 96.6(1) and 96.3(1)°). Bond angles and distances within the ligand are comparable and normal. Both I and II show the SCN^- to be ionic and not involved in the coordination sphere of Pd. In II, each SCN^- exhibits two weak hydrogen bonds (N·····H–N) (N3–N1, 3.015(4) Å; N3–N2, 3.050(4) Å) to hydrogens bound to the ligating amino groups. There are no Pd–(SCN) distances less than 3.5 Å. In I, the SCN^- anions are situated with the C≡N atoms equidistant from Pd (3.505(7) and 3.529(6) Å, respectively). There are no hydrogen bonded interactions.

Because of the poor solubility of the complexes in methanol, acetone and methylene chloride, the DMF solution data are, by far, the most informative with regard to the bonding mode trends exhibited by the complexes in solution. Here, the effects due to steric hindrance become readily apparent. All of the diamines containing two tertiary amines [$et(morph)_2$, $et(pip)_2$, $et(pyrr)_2$ $et(N(CH_3)_2)_2$, $pr(N(CH_3)_2)_2$], *i.e.*, those which create the greatest steric hindrance, give rise to solely N-bound thiocyanates. As might be expected, the diamines containing one tertiary amine with very bulky groups [$et(morph)NH_2$, $et(pyrr)NH_2$, $et(pip)NH_2$] yield both bonding modes. The data do not permit distinguishing between a mixture of di-N- and di-S-bound species and a mono-N-mono-S-bound complex in these cases, although the latter is more probable, considering the structures of these ligands. The remaining diamines, being the least sterically demanding, yield S-bound [$et(NH(C_6H_5))_2$, $bz(NH_2)_2$] or, as noted above, ionic thiocyanates. The trends

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*Tables of supplementary data available from the authors on request.

TABLE VI. Molar Conductance, Thiocyanate $^{13}C\{^1H\}$ NMR and Electronic Spectral Data for DMF Solutions of the [Pd(substituted diamine)(thiocyanate)$_2$] Complexes.

Diamine	Λ_m (ohm^{-1} cm^2 mol^{-1})	Thiocyanate δ ^{13}C(ppm)[c]	λ_{max}, kK (log ϵ)
et(morph)$_2$	22.5[a]	139.2 (N)	34.6 (4.99), 28.2 (4.10)
et(pip)$_2$	15.8[a]	[e]	37.9 (4.95), 36.1 (4.91), 29.2 (4.34)
et(pyrr)$_2$	13.2[a]	[d]	38.0 (4.95), 29.2 (4.24)
et(N(CH$_3$)$_2$)$_2$	~0a	[e]	37.0 (4.99), 27.8 (4.00)
et(NH$_2$)$_2$(CH$_3$)$_2$	69.7[b]	131.79 (ionic)	38.0 (4.24), 35.3 (3.86)
et(NH(C$_6$H$_5$))$_2$	19.7[a]	121.33 (S)	37.9 (5.11), 33.2 (5.17)
et(NHCH$_3$)$_2$	86.6[b]	132.33 (ionic)	38.6 (4.15), 32.2 (3.68)
pr(N(CH$_3$)$_2$)$_2$	~0[a]	[e]	38.2 (5.19), 32.9 (4.60)
et(NH$_2$)(N(CH$_3$)$_2$)	86.9[b]	132.14 (ionic)	38.6 (4.20), 33.9 (3.79)
pyNH$_2$	51.2[b]	[d]	37.6 (5.24)
et(morph)NH$_2$	13.5[a]	118.96 (S)	37.5 (5.14), 28.5 (4.19)
et(pyrr)NH$_2$	13.0[a]	119.1 (S)	38.5 (4.43), 34.2 (3.63)
et(pip)NH$_2$	12.5[a]	[e]	37.9 (5.23), 28.6 (4.15)
bz(NH$_2$)$_2$	13.6[a]	118.96 (S)	37.5 (5.13)

[a] Non-electrolyte. [b] Electrolyte. [c] Bonding mode in parentheses. [d] Insufficient solubility. [e] Not observed.

observed in the other solvents, where the data are available, are similar. The major difference involves the aforementioned greater tendency toward S-bonding exhibited by the methanol solutions. In general, as has previously been observed [2, 3], the ν_{CN} integrated absorption intensity values were found to increase in the order Pd–SCN < SCN$^-$ < Pd–NCS.

Without exception, the molar conductance values shown in Table VI for DMF solutions of the complexes mirror the thiocyanate bonding mode conclusions (ionic *versus* coordinated) reached on the basis of the IR spectral evidence for these solutions. [It should be noted that the molar conductance values observed for the ionic complexes fall somewhat below the range previously reported [19] for 1:2 electrolytes in DMF, being more comparable to the values cited [19] for 1:1 electrolytes.] Likewise, the thiocyanate ^{13}C data shown in Table VI, where available, also tend to buttress [22] these conclusions.

Unfortunately, the solubility of half of the complexes was too low to permit the acquisition of their thiocyanate ^{13}C chemical shifts. In addition, the acquisition of ^{13}C NMR data was made more difficult by the dynamic range of the NMR spectrometer. The region where the thiocyanate resonances occur is flanked by strong resonances from the DMF solvent. A weak thiocyanate carbon resonance would be discerned as noise by the instrument and subsequently suppressed. Operating the machine in a proton-coupled mode could potentially have helped the situation, but, unfortunately, only half of the total number of complexes exhibited thiocyanate carbon resonances, even under these conditions.

The formation of [Pd(et(pyrr)NH$_2$)$_2$](SCN)$_2$ (structure II, Fig. 3) in the attempted recrystallization of [Pd(et(pyrr)NH$_2$)(SCN)$_2$] from DMF solution undoubtedly results from the following reaction:

$$2[\mathrm{Pd(et(pyrr)NH_2)(SCN)_2}] + 4\ \mathrm{DMF} \rightleftharpoons$$

$$[\mathrm{Pd(et(pyrr)NH_2)_2}](\mathrm{SCN})_2 + [\mathrm{Pd(DMF)_4}](\mathrm{SCN})_2$$

This conclusion is supported by the observation that the thiocyanate ^{13}C resonance observed at 119.1 ppm for a freshly prepared solution of [Pd(et(pyrr)-NH$_2$)(SCN)$_2$] (see Table VI) disappeared after the solution had been warmed for 2 weeks in an NMR tube. It was replaced by a new ^{13}C resonance at 131.5 ppm which is characteristic [22] of ionic SCN$^-$, as would be expected to be present in the final product mixture. It seems likely that many of the [Pd(substituted diamine)(thiocyanate)$_2$] complexes would also undergo this type of transformation when warmed in DMF. Related rearrangements have previously been observed [9, 23] for a variety of Pd(II) thiocyanate complexes in DMF solution.

The electronic spectral data shown for the complexes in Table VI reveal that the energy of the longest wavelength absorption band tends to be higher for the $[Pd(diamine)_2](SCN)_2$ complexes. This would be expected on the basis of the ligand field strengths of the diamines being greater than that of either S- or N-bound thiocyanate.

In summary, the data obtained for the complexes prepared and characterized in this study clearly demonstrate that increasing steric hindrance created by the diamines tends to promote N-bonding on the part of the thiocyanates. The actual thiocyanate bonding mode observed for a given complex is, however, also influenced by the physical state of the complex (solid *versus* solution), kinetic factors and the nature of the solvent in which the complex is prepared and/or characterized.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the research carried out at the University of Delaware through grant #9680-AC3.

References

1 F. Basolo, W. H. Baddley and J. L. Burmeister, *Inorg. Chem., 3,* 1202 (1964).

2 J. L. Burmeister, in 'The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives', A. A. Newman, Ed., Academic Press, London, 1975, pp. 68–130.

3 A. H. Norbury, *Adv. Inorg. Chem. Radiochem., 17,* 231 (1975).

4 A. J. Carty, *Inorg. Chem., 15,* 1956 (1976).

5 S. J. Anderson, P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. Dalton,* 1959 (1976).

6 W. L. Steffen and G. J. Palenik, *Inorg. Chem., 15,* 2432 (1976).

7 S. J. Anderson and R. J. Goodfellow, *J. Chem. Soc. Dalton,* 1683 (1977).

8 J. J. MacDougall, J. H. Nelson, M. W. Babich, C. C. Fuller and R. A. Jacobson, *Inorg. Chim. Acta, 27,* 201 (1978).

9 G. P. McQuillan and I. A. Oxton, *J. Chem. Soc. Dalton,* 1460 (1978).

10 J. J. MacDougall, A. W. Verstuyft, L. W. Cary and J. H. Nelson, *Inorg. Chem., 19,* 1036 (1980).

11 J. J. MacDougall, E. M. Holt, P. DeMeester, N. W. Alcock, F. Mathey and J. H. Nelson, *Inorg. Chem., 19,* 1439 (1980).

12 A. Gero, *J. Am. Chem. Soc., 76,* 5158 (1954).

13 A. L. Lott, III, *Inorg. Chem., 13,* 667 (1974).

14 R. L. Hassel, *Ph.D. Dissertation,* University of Delaware, 1973.

15 D. A. Ramsay, *J. Am. Chem. Soc., 74,* 72 (1952).

16 W. C. Fultz, J. L. Burmeister, J. J. MacDougall and J. H. Nelson, *Inorg. Chem., 19,* 1085 (1980).

17 R. A. Bailey, T. W. Michelsen and W. N. Mills, *J. Inorg. Nucl. Chem., 33,* 3206 (1971).

18 A. W. Verstuyft, *Ph.D. Dissertation,* University of Nevada, Reno, 1975, p. 311.

19 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

20 J. L. Burmeister, R. L. Hassel and R. J. Phelan, *Inorg. Chem., 10,* 2032 (1971).

21 W. C. Fultz, J. L. Burmeister, C. P. Cheng and T. L. Brown, *Inorg. Chem., 20,* 1734 (1981).

22 J. A. Kargol, R. W. Crecely and J. L. Burmeister, *Inorg. Chem., 18,* 2032 (1979).

23 W. Levison and C. A. McAuliffe, *J. Chem. Soc. Dalton,* 2238 (1974).