

Coordination Behavior of Thiocyanate in the Complexes $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{M}(\text{CNS})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$)

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The complexes $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{M}(\text{CNS})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) have been prepared and characterized. The structures of these complexes are markedly metal ion and physical state dependent. All of the complexes are square planar. In the solid state the nickel complex is $\text{trans-L}_2\text{M}(\text{NCS})_2$ (by crystal structure analysis), the palladium complex is $\text{trans-L}_2\text{Pd}(\text{SCN})_2$ and the platinum complex is $\text{cis-L}_2\text{Pt}(\text{NCS})_2$ (both determined by infrared spectroscopy, including integrated intensity measurements). Fourier transform phosphorus nmr spectra on chloroform solutions at ambient temperature indicate that for the platinum complex, all six possible isomers are present in solution in the relative ratios: $\text{trans-L}_2\text{Pt}(\text{NCS})_2$: $\text{trans-L}_2\text{Pt}(\text{SCN})(\text{NCS})$: $\text{trans-L}_2\text{Pt}(\text{SCN})_2$: $\text{cis-L}_2\text{Pt}(\text{NCS})_2$: $\text{cis-L}_2\text{Pt}(\text{SCN})_2$: $\text{cis-L}_2\text{Pt}(\text{SCN})(\text{NCS})$: 0.38:0.57:0.38:0.34:0.28:1, respectively. For the palladium complex, under similar conditions, all of the isomers but $\text{cis-L}_2\text{Pd}(\text{SCN})(\text{NCS})$ are present, with $\text{trans-L}_2\text{Pd}(\text{NCS})_2$ and $\text{cis-L}_2\text{Pd}(\text{NCS})_2$ predominant in a ratio of 0.15:1, respectively. The relative population of cis isomers decreases in the sequence $\text{Pd} > \text{Pt} > \text{Ni}$, and the relative population of mixed linkage isomers decreases in the sequence $\text{Pt} > \text{Pd} > \text{Ni}$. The differences in the structures are discussed in light of current theories.

Introduction

Recently, there has been increasing interest, [3–15], including considerable fascination and no little controversy [6, 7], in the ambidentate bonding capabilities of the thiocyanate ion (CNS^-). This interest has been caused by this ion's ability, under various conditions, to coordinate to metals through the nitrogen atom, through the sulfur atom or through both as a bridging species. It has variably been proposed that steric effects [6, 16], electronic effects [17, 18] or a combination thereof [5, 7] predominantly determine the thiocyanate bonding mode. In the past, the d^8 transition metals, specifically nickel, palladium and platinum, have been most often

selected to probe this bonding behavior [3–15]. Among studies of the complexes possessing the general formula L_2MX_2 to date, the nickel complexes have also evoked considerable interest because they exhibit interesting structural isomerism (square planar and tetrahedral). When $\text{X} = \text{CNS}^-$ these nickel complexes are invariably *trans*-square planar with the thiocyanate being N-bound [5]. When X is a halide, equilibrium mixtures [19] of square planar and tetrahedral complexes result, even in the solid state. Similar L_2MX_2 palladium and platinum complexes exhibit mixtures of *cis*- and *trans*-square planar isomers in solution.

Therefore, the potential for several geometries exists among the L_2MX_2 complexes of the metals in the nickel triad. To date there have been very few studies on isoelectronic, potentially isostructural thiocyanate complexes of these three metals. It has been demonstrated from the plethora of investigations [5] of these types of complexes that in the nickel complexes, the thiocyanate is N bound but palladium and platinum are schizophrenic, exhibiting both bonding modes, often simultaneously in a single complex. This schizophrenia seems to be more prevalent for palladium than for platinum and it seems that the palladium complexes are generally the most sensitive to minor effects on the bonding mode of the thiocyanate anion. In an effort to extend the present knowledge concerning the effects of the thiocyanate anion on the structures of d^8 metal complexes and of the metal on the thiocyanate bonding mode, we have prepared the homologous series of nickel triad metal complexes having the general formula $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{M}(\text{CNS})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$). Studies have been conducted taking into consideration both solid state and solution structures. The results of these studies are reported herein.

Experimental

Chemicals used were reagent grade and were used as received, or were synthesized by standard methods.

TABLE I. Physical Properties and Infrared Spectral Data^a for the Complexes, (MePPh₂)₂M(CNS)₂.

M	Color	MP °C	State	ν_{CN} (cm ⁻¹)	$\Delta\nu_{1/2}$ (cm ⁻¹)	$A (\times 10^{-4} M^{-1} \text{ cm}^{-2})$ or ISR^a	ν_{CS} (cm ⁻¹)	δ_{NCS} (cm ⁻¹)	ν_{ML} (cm ⁻¹)	
Ni	Red	176	Nujol	2110	38	1.92	862	485	351	N-bound
Ni	Red		CHCl ₃	2098	35	20	862	—	—	N-bound
Pd	Yellow	219	Nujol	2115	22	0.30	755	458	315	S-bound
Pd	Yellow		CHCl ₃	2085	58	14.9	—	—	—	N-bound
Pt	Yellow	226	Nujol	2100, 2118	35, 20	1.16	755, 880	447, 438	314, 303	S-bound
Pt	Yellow		CHCl ₃	2090	52	8.2	880	—	—	N-bound

ISR = internal standard ratio referenced to salicylic acid.

^aSee R. A. Bailey, S. I. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971); R. A. Bailey, T. W. Michelsen and W. N. Mills, *J. Inorg. Nucl. Chem.*, **33**, 3206 (1971).

The complexes were synthesized by metathesis of the corresponding chloro complexes [23] with KSCN in methanol/chloroform. The physical data for the complexes are given in Table I. Melting points were determined on a Meltemp melting point apparatus and are uncorrected. Satisfactory elemental analyses were obtained for each complex by Chemalytics, Tempe, Arizona.

Infrared and nmr spectra were obtained as described previously [24]. Integrated intensities of the CN stretching absorptions were determined by literature methods [25].

Crystal Data

Well formed dark red crystals of Ni(NCS)₂(PPh₂-Me)₂ were grown from chloroform by slow evaporation. A crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm was selected. Preliminary oscillation photographs indicated that the compound crystallized in the triclinic crystal system. Final unit-cell parameters, obtained from a least-squares fit of $\pm 2\theta$ values for fourteen independent reflections (MoK α radiation, $\lambda = 0.70954$ Å) at 25 °C, yielded $a = 9.862 \pm 0.023$ Å, $b = 11.041 \pm 0.023$ Å, $c = 6.988 \pm 0.016$ Å, $\alpha = 99.98 \pm 0.22^\circ$, $\beta = 97.45 \pm 0.22^\circ$, $\gamma = 109.21 \pm 0.20^\circ$, triclinic, P1.

Collection and Reduction of X-Ray Intensity Data

The crystal was mounted using nail polish as glue on a copper wire and placed in a goniometer head. Data were collected at room temperature using a technique described by Rohrbach and Jacobson [26]. Within a 2θ sphere of 68° ($\sin \theta/\lambda = 0.79$ Å⁻¹) all data (6164 reflections) in four octants were measured using an ω -scan technique. Of these, 2939 were considered observed ($>3.0 \sigma_{F_0}$). The intensity data were not corrected for absorption due to the small absorption factor $\mu = 9.37$ cm⁻¹. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_t + C_b + (0.03C_t)^2 + (0.03C_b)^2 + (0.03C_n)^2,$$

where C_t , C_b , and C_n are the total count, background count, and net count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method [27]. Equivalent data were averaged, yielding 2755 independent data.

Solution and Refinement of Structure

Statistical tests indicated the presence of a center of symmetry. The occurrence of one molecule per cell ($d_{\text{calc}} = 1.37$ g/cc) implied that the position of the nickel atom was restricted by space group symmetry to be at the origin. The positions of the remaining atoms were found by successive structure factor [28] and electron density map [29] calculations. In addition to positional parameters, the aniso-

TABLE II (a). Positional Parameters^a for Ni(NCS)₂(PPh₂-Me)₂.

Atom	x	y	z
Ni	0	0	0
S	3102(2) ^b	1802(2)	6006(2)
P	-305(1)	1904(1)	-166(2)
N	1158(5)	713(4)	2429(7)
C	1971(5)	1181(5)	3940(7)
Me	-388(7)	2286(7)	-2579(9)
C11	-1996(5)	1888(4)	575(7)
C12	-2532(6)	1136(6)	1853(10)
C13	-3836(7)	1102(8)	2461(12)
C14	-4601(6)	1812(7)	1715(11)
C15	-4070(7)	2574(8)	440(11)
C16	-2785(6)	2609(6)	-140(9)
C21	1128(5)	3326(4)	1430(7)
C22	938(6)	3978(6)	3192(9)
C23	2102(7)	5009(6)	4451(10)
C24	3435(6)	5399(5)	3956(9)
C25	3653(6)	4756(6)	2234(10)
C26	2515(6)	3727(6)	967(9)
H1	-39(7)	323(7)	-235(10)
H2	48(8)	220(7)	-302(10)
H3	-122(8)	157(7)	-350(11)
H12	-199(7)	63(7)	233(10)
H13	-429(8)	36(7)	327(11)
H14	-557(8)	182(6)	210(10)
H15	-464(8)	308(6)	15(10)
H16	-233(7)	323(7)	-112(11)
H22	0(8)	371(6)	350(10)
H23	189(7)	546(7)	555(11)
H24	426(7)	617(7)	488(10)
H25	461(8)	503(6)	193(10)
H26	273(7)	316(7)	-27(11)

^aThe positional parameters are in fractional unit cell coordinates ($\times 10^4$), except for hydrogens ($\times 10^3$). ^bIn this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

tropic thermal parameters for all non-hydrogen atoms were refined by a full-matrix least squares procedure, minimizing the function $\sum \omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$, to a final conventional discrepancy factor $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 7.5\%$. The scattering factors used were those of Hanson *et al.* [30], modified for the real and imaginary parts of anomalous dispersion [31].

The final positional and thermal parameters are listed in Table II. The standard deviations were calculated from the inverse matrix of the final least-squares cycle [32]. Bond lengths and bond angles are listed in Tables III and IV, respectively and an ORTEP drawing of the molecule is given in Figure 1 [33].

Results and Discussion

There are six possible square planar isomers for the complexes $L_2M(CNS)_2$, viz. *cis* and *trans* N-bound, *cis* and *trans* S-bound and *cis* and *trans* mixed linkage isomers and three possible analogous tetrahedral isomers. The nickel complex exhibits only one of these possibilities both in solution and in the solid state, that being *trans*- $L_2Ni(NCS)_2$. The solution infrared data (Table I) are in agreement with the solid state infrared data in supporting this conclusion. Unfortunately, this conclusion could not be supported by solution nmr data due to the combination of limited solubility and the presence of some paramagnetic material in solution. Because of this difficulty and the inherent uncertainties in the infrared criteria for the structures of complexes of this type [5], an X-ray structure determination was performed on this complex, the details of which are given in Tables II–IV and Figure 1. Structural data on similar nickel complexes containing either phosphines or the thiocyanate ion are listed in Table V.

There are several interesting points regarding the structure of $[CH_3P(C_6H_5)_2]_2Ni(NCS)_2$. Although not required by steric or other apparent reasons, the complex has an exact center of symmetry. The SCN–Ni–NCS moiety is also linear within experimental error. In fact this seems to be unique among the complexes listed in Table V. All other nickel thiocyanate complexes display Ni–N–C angles which are significantly less than 180° . This complex also possesses the shortest Ni–N bond length of the thiocyanate complexes while the Ni–P bond length appears to be normal.

The following points concerning the data in Table V should be noted:

1. The nickel–phosphorus bond lengths span the limited range of 2.14–2.18 Å (a 6% change) while the nickel–halogen or pseudo-halogen bond lengths span a much greater range 1.69–2.55 Å (a 34% change). Even the Ni–N bond lengths in the isothiocyanate complexes change from 1.8–2.15 Å (a 16% change).

2. The P–Ni–X angles vary considerably from 87.8 – 110.4° .

3. The Ni–N=C bond angles change considerably from 140 to 176.1° .

4. The coordination geometry and coordination numbers are variable and encompass square planar and tetrahedral (4 coordinate), trigonal bipyramidal and square based pyramidal (5 coordinate), and pseudo octahedral (6 coordinate).

Thus the possibility for manifestation of steric effects on the thiocyanate bonding mode and on the coordination geometry can be clearly established by determining the particular structure, angles and distances adopted. It seems imminently clear that, for nickel, when steric effects become important they are accommodated by a change in coordination number

TABLE II (b). Thermal Parameters^a for Ni(NCS)₂(PPh₂Me)₂.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	101(1)	98(1)	216(2)	36(1)	-2(1)	10(1)
S	141(2)	173(2)	228(3)	17(1)	-14(2)	27(2)
P	102(1)	98(1)	216(3)	36(1)	17(1)	27(1)
N	138(5)	110(4)	263(10)	43(4)	-25(6)	1(5)
C	118(5)	104(5)	249(12)	28(4)	20(6)	28(6)
Me	169(8)	150(7)	248(13)	62(6)	43(8)	50(7)
C11	105(5)	108(5)	249(11)	37(4)	19(9)	23(6)
C12	141(7)	144(6)	359(17)	46(5)	84(9)	74(8)
C13	159(8)	187(9)	397(20)	35(7)	112(11)	52(11)
C14	108(6)	179(8)	417(20)	45(6)	48(9)	-11(10)
C15	142(7)	225(10)	383(19)	103(7)	48(10)	60(11)
C16	146(7)	179(8)	317(15)	85(6)	53(8)	69(9)
C21	110(5)	99(4)	256(11)	39(4)	28(6)	37(6)
C22	117(6)	135(6)	308(14)	28(5)	38(7)	2(7)
C23	158(8)	153(7)	314(16)	41(6)	24(9)	-38(8)
C24	131(6)	108(5)	359(17)	26(5)	14(8)	7(7)
C25	120(6)	131(6)	382(18)	12(5)	35(8)	26(8)
C26	127(6)	143(6)	311(15)	33(5)	45(8)	13(8)

^aThe β_{ij} are defined by: $T = \exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. For all hydrogen atoms an isotropic thermal parameter of $4.0 \text{ \AA}^2$ was assigned.

TABLE III. Bond Distances (Å) for Ni(NCS)₂(PPh₂Me)₂.

Ni-N	1.802(4)	C24-C25	1.367(9)
Ni-P	2.240(1)	C25-C26	1.374(8)
N-C	1.159(7)	C26-C21	1.392(7)
C-S	1.592(7)	Me-H1	1.03(7)
P-Me	1.806(6)	Me-H2	0.98(7)
P-C11	1.805(5)	Me-H3	0.99(7)
P-C21	1.798(4)	C12-H12	0.96(6)
C11-C12	1.363(8)	C13-H13	1.08(7)
C12-C13	1.397(9)	C14-H14	1.03(6)
C13-C14	1.372(11)	C15-H15	0.94(7)
C14-C15	1.366(10)	C16-H16	1.09(7)
C15-C16	1.371(8)	C22-H22	0.94(7)
C16-C11	1.390(8)	C23-H23	0.93(7)
C21-C22	1.382(8)	C24-H24	1.01(7)
C22-C23	1.386(8)	C25-H25	0.95(7)
C23-C24	1.353(8)	C26-H26	1.07(7)

or geometry and not by a change in thiocyanate bonding mode. In short, nickel remains a hard acid in spite of steric effects and one must conclude that electronic effects are more important in determining the thiocyanate bonding mode to nickel than are steric effects.

The palladium complex $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Pd}(\text{NCS})_2$ appears [25], from infrared data (Table I), to exist as a single isomer in the solid state; that being *trans*-L₂Pd(SCN)₂. Upon dissolution in chloroform the infrared data suggest that at least the predominant species is *trans*-L₂Pd(NCS)₂, which in turn suggests that linkage isomerization occurs upon

TABLE IV. Bond Angles (Deg.) for Ni(NCS)₂(PPh₂Me)₂.

P-Ni-N	91.6(3)	H12-C12-C11	118(4)
Ni-N-C	176.1(5)	H12-C12-C13	121(4)
N-C-S	178.8(8)	H13-C13-C12	117(4)
Ni-P-Me	115.8(3)	H13-C13-C14	123(3)
Ni-P-C11	109.7(2)	H14-C14-C13	123(4)
Ni-P-C21	113.6(2)	H14-C14-C15	117(4)
Me-P-C11	106.3(3)	H15-C15-C14	112(4)
Me-P-C21	104.0(4)	H15-C15-C16	128(4)
C11-P-C21	106.6(3)	H16-C16-C15	121(3)
P-C11-C12	119.3(4)	H16-C16-C11	118(3)
P-C11-C16	122.0(4)	H22-C22-C21	118(4)
C16-C11-C12	118.7(5)	H22-C22-C23	121(4)
C11-C12-C13	120.9(7)	H23-C23-C22	117(4)
C12-C13-C14	119.2(7)	H23-C23-C24	123(4)
C13-C14-C15	120.4(6)	H24-C24-C23	119(4)
C14-C15-C16	120.0(6)	H24-C24-C25	121(4)
C15-C16-C11	120.8(6)	H25-C25-C24	119(4)
P-C21-C22	122.3(4)	H25-C25-C26	120(4)
P-C21-C26	119.2(4)	H26-C26-C25	120(4)
C26-C21-C22	118.3(5)	H26-C26-C21	120(4)
C21-C22-C23	120.5(6)	P-Me-H1	105(4)
C22-C23-C24	120.2(6)	P-Me-H2	105(4)
C23-C24-C25	120.3(6)	P-Me-H3	108(4)
C24-C25-C26	120.5(6)	H1-Me-H2	114(5)
C25-C26-C21	120.2(6)	H1-Me-H3	119(5)
		H2-Me-H3	105(6)

dissolution. The proton nmr spectra are of little assistance in assigning the solution structure, as two broad singlets appear for the P-CH₃ resonances at δ 2.03 and δ 2.23 and neither resonance clearly shows evi-

TABLE V. Representative Crystal Structure Data for Nickel Complexes.

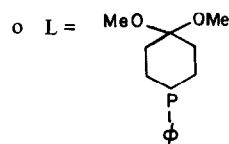
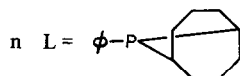
Compound	Ni-P (Å)	Ni-X (Å)	∠PNiX (°)	∠NiNC (°)	Reference
NiBr ₂ (PEt ₃) ₂	2.26	2.30	90.31	—	a
Ni(CN) ₂ (PMe ₂ Ph) ₃	2.223–2.261	1.836, 1.860	87.8–92.4	—	b
NiCl ₂ (PPh ₃) ₂	2.28	2.27	—	—	c
NiBr ₂ (PPh ₃) ₂	2.323, 2.343	2.346, 2.329	101.8–108.3	—	d
NiBr ₂ (PBzPh ₂) ₂	2.263	2.305	92.7	—	e
Ni(NCS) ₂ (PMePh ₂) ₂	2.240	1.802	91.6	176.1	f
Ni(NCS) ₂ (en) ₂	—	2.15	—	140.0	g
Ni(NCS) ₂ (SC(NH ₂) ₂) ₂	—	1.992(7)	—	162.2	h
Ni(NCS) ₂ (H ₂ NCSNHNH ₂) ₂	—	2.04	89.9	175.0	i
Ni(NCS) ₂ (CH ₅ N ₃ S) ₂	—	2.05	—	173.3	j
NiBr ₂ (PMe ₃) ₃	2.19–2.21 ^u 2.20–2.21 ^v	2.451, 2.553 ^u 2.426, 2.580 ^v	86.5–134.5 ^u 86.3–132.3 ^v	—	k
NiBr ₂ ((Bu ^t) ₂ PF) ₂	2.232	2.288	92.0	—	l
NiBr(σC ₆ F ₅)(PPh ₂ Me) ₂	2.2164, 2.2148	2.3245 ^w 1.8800 ^x	89.09–89.57 ^w 90.54–91.02 ^x	—	m
NiCl ₂ (C ₈ H ₁₄ PPh) ₂	2.227	2.166	90.29	—	n
NiCl ₂ (C ₇ H ₁₄ O ₂ PPh) ₂	2.254, 2.245	2.175, 2.167	87.6–92.4	—	o
α-Ni(trien)(NCS) ₂	—	2.083	—	171.5	p
[Ni(N ₃ P)Br]PBh ₄	2.141	2.298	89.7	—	q
NO(N ₃)(NO)(PPh ₃) ₂	2.306, 2.257	2.02 ^y 1.69 ^z	95.3–102.4 ^y 101.1–110.4 ^z	—	r
[Ni(bdma)NCS]PF ₆	2.206	1.848	—	168.5	s

^aG. Giacometti, V. Scatturin and A. Turco, *Gazz. Chim. Ital.*, **88**, 434 (1958). ^bJ. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1090 (1969). ^cG. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963). ^dJ. A. J. Jarvis, R. H. B. Mais and P. G. Owston, *J. Chem. Soc. A*, 1473 (1968). ^eSquare Planar Form: B. T. Kilbourn, H. M. Powell and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963). Tetrahedral form: B. T. Kilbourn, H. M. Powell and J. A. C. Darbyshire, *J. Chem. Soc. A*, 1688 (1971). ^fThis work. ^gB. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963). ^hM. Nardelli, F. Gasparri, G. G. Battistini and P. Domiano, *Acta Cryst.*, **20**, 349 (1966). ⁱJ. Garaj and M. Dumaj-Jurco, *Chem. Comm.*, 518 (1968). ^jM. Dunaj-Jurco, J. Garaj and A. Sirota, *Coll. Czech. Chem. Comm.*, **39**, 236 (1974). ^kH. B. Gray *et al.*, *J. Am. Chem. Soc.*, **96**, 4428 (1974). ^lW. S. Sheldrick and O. Stelzer, *J. Chem. Soc. Dalton*, 926 (1973). ^mM. R. Churchill, K. L. Kalra and M. V. Veidis, *Inorg. Chem.*, **12**, 1656 (1973). ⁿA. E. Smith, *Inorg. Chem.*, **11**, 3017 (1972). ^oA. T. McPhail and J. C. H. Steele, *J. Chem. Soc. Dalton*, 2680 (1972). ^pA. Clausen and A. C. Hazell, *Acta Chem. Scand.*, **24**, 2811 (1970). ^qI. Bertini, P. Dapporto, G. Fallani and L. Sacconi, *Inorg. Chem.*, **10**, 1703 (1971). ^rJ. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971). ^sA. Bianchi and C. A. Ghilardi, *J. Chem. Soc. A*, 1096 (1971). ^{u,v}Complex exists as two discrete trigonal bipyramidal structures in the crystal lattice. ^wX = Br. ^xX = C₆H₅. ^yX = N₃. ^zX = NO.

Notation used:

Reference

j CH₅N₃S = thiosemicarbazide



p trien = NH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂

q PN₃ = bis(2-ethylaminoethyl)(2-diphenylphosphinoethyl)amine

s bdma = (Ph₂PCH₂CH₂)₂NCH₂OCH₃

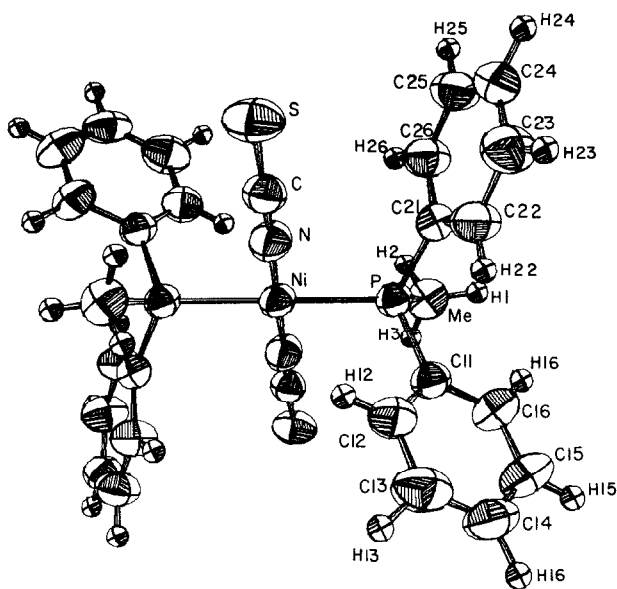


Figure 1. The $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Ni}(\text{NCS})_2$ molecule showing 50% probability ellipsoids; 30% for hydrogen.

dence of spin coupling. The proton spectrum does, however, indicate that more than one species is present in solution. The ^{31}P nmr spectra give much more information. They demonstrate that five isomers are present in CDCl_3 solution. The ^{31}P chemical shifts (relative intensities) and assignments are as follows: $-\delta 16.47(0.17)$ *cis*- $\text{L}_2\text{Pd}(\text{SCN})_2$, $-\delta 11.53(1)$ *cis*- $\text{L}_2\text{Pd}(\text{NCS})_2$, $-\delta 8.81(0.15)$ *trans*- $\text{L}_2\text{Pd}(\text{NCS})_2$, $-\delta 6.59(0.017)$ *trans*- $\text{L}_2\text{Pd}(\text{SCN})(\text{NCS})$ and $-\delta 2.89(0.023)$ *trans*- $\text{L}_2\text{Pd}(\text{SCN})_2$. These assignments were made using the relationships noted elsewhere [10, 15, 34] for ^{31}P chemical shifts for similar complexes. Thus the ^{31}P data agree with the infrared data regarding the predominant bonding mode (NCS), but the infrared data is unable to distinguish between the *cis* and *trans* geometries. The lack of apparent spin coupling in the proton nmr spectra is then explained on the basis of the P- CH_3 resonances being the superposition of virtually coupled multiplets, representing the five isomers.

The platinum complex appears from infrared [25] data (Table I), to be a single isomer in the solid state, that being *cis*- $\text{L}_2\text{Pt}(\text{NCS})_2$. The solution infrared data suggest that the thiocyanate is nitrogen bound but that the dominant species is *trans*- $\text{L}_2\text{Pt}(\text{NCS})_2$. Thus upon dissolution in chloroform, geometric isomerization without linkage isomerization is indicated by the infrared data. The proton nmr spectra in CDCl_3 exhibit three 1:2:1 triplets for the P- CH_3 resonances, representing three distinct *trans* isomers at $\delta 2.36$, 2.22 and 2.12 with $|^2J_{\text{PH}} + ^4J_{\text{PH}}| = 7$ Hz for each triplet and a broad unresolved multiplet centered at $\delta 1.90$ representing an indeterminate

number of *cis* isomers. Once again the ^{31}P nmr spectra provide much more information. They clearly demonstrate the presence of all six possible isomers. The ^{31}P chemical shifts (relative intensities) $J_{\text{Pt-P}}$ coupling constants and assignments are: $-\delta 7.33(0.38)$, 2450, *trans*- $\text{L}_2\text{Pt}(\text{NCS})_2$; $-\delta 5.36(0.57)$, 2395, *trans*- $\text{L}_2\text{Pt}(\text{NCS})(\text{SCN})$; $-\delta 3.48(0.38)$, 2345, *trans*- $\text{L}_2\text{Pt}(\text{SCN})_2$; $-\delta 3.09(0.34)$, 3410, *cis*- $\text{L}_2\text{Pt}(\text{NCS})_2$; $-\delta 2.59(0.28)$, 3500, *cis*- $\text{L}_2\text{Pt}(\text{SCN})_2$ and an AB quartet with δ_A 7.19 and δ_B 10.83, $J_{\text{Pt-P}}$ not observed and $^2J_{\text{PP}} = 30$ with relative intensity of 1. Thus the bonding mode in CDCl_3 , as determined by ^{31}P nmr, is approximately equally divided between N-bound and S-bound and the geometry is approximately half *cis* and half *trans*. However the infrared data indicates only N-bound thiocyanate and *trans* geometry. This is a clear indication of the pitfalls in relying on infrared criteria for structural assignments of complexes of this type. The ^{31}P assignments are made using the relationships noted elsewhere [10, 12, 15, 34] for ^{31}P chemical shifts, the geometry dependence [35] of $^2J_{\text{PP}}$ and the geometry relationships [36] of $J_{\text{Pt-P}}$.

Though it is clear, from the number of isomers present in solutions of the palladium and platinum complexes, that a detailed solvent study would yield valuable information, this has not been attempted for these two complexes because of limited solubility. Studies of this type are being completed on similar but more soluble complexes and the results will be reported in a future publication.

It is noted from the above data that the relative isomer populations in solution are markedly metal-dependent. The *cis* isomer population decreases in the sequence $\text{Pd} > \text{Pt} > \text{Ni}$ and the mixed linkage isomer population decreases in the sequence $\text{Pt} > \text{Pd} > \text{Ni}$. Another important observation to consider in attempting to rationalize the above behavior is that for an analogous complex [21] $[\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2]_2\text{-Pd}(\text{NCO})_2$, only two isomers are present in CDCl_3 solution, namely *cis* and *trans* $\text{L}_2\text{Pd}(\text{NCO})_2$ in the relative ratio of 0.11:1. Under the same conditions, the ratio of *cis* and *trans* $\text{L}_2\text{Pd}(\text{NCS})_2$ is 1:0.15, respectively. Thus, for palladium, changing the anion from NCO^- to NCS^- causes a complete inversion in the relative isomer stabilities. For a similar platinum complex [12] $[\text{CH}_3\text{P}(\text{C}_2\text{H}_5)_2]_2\text{Pt}(\text{NCO})_2$, only the *cis* isomer is observed in solution. On the other hand with $\text{L}_2\text{Pt}(\text{CNS})_2$ we find that the *cis* and *trans* isomers have approximately equal abundances.

In attempting to assess the relative importance of factors influencing the structures of the $\text{L}_2\text{M}(\text{CNS})_2$ complexes, the following points should be considered. 1) Ni^{2+} is intrinsically "hard" while Pd^{2+} and Pt^{2+} are intrinsically "soft". Thus, in the absence of other effects [5], nickel should favor M-NCS bonding whereas palladium and platinum should favor M-SCN bonding as is found [5] for the isoleptic complexes,

$[M(CNS)_4]^{2-}$. 2) Steric effects on the CNS bonding mode are maximized in the *trans* isomers and anti-symbiotic electronic effects are maximized in the *cis* isomers. Thus steric effects favor the *trans* isomers and N-bonding, and electronic effects favor the *cis* isomers and N-bonding if L is a phosphine [4], or S-bonding if L is an amine [4]. 3) For the isomerization process $cis-L_2M(SCN)_2 = trans-L_2M(SCN)_2$ or $cis-L_2M(NCS)_2 = trans-L_2M(NCS)_2$ in solution, ΔH_{bond} [20, 21] and $\Delta H_{solvation}$ [20, 21] should favor the *trans* isomers. ΔS will be more important for the S-bound pair than for the less polar N-bound pair. We have consistently shown that, for palladium complexes, the isomerization process is entropy controlled (but see reference 21) and that the major contributors to ΔH and ΔS are the solvation terms [20]. It is for these reasons that the more polar [4] NCS ion reverses the predominant geometry relative to NCO in the two palladium complex. 4) Internal bond energies will be dependent upon the σ -donor- π -acceptor properties, *trans* influences of the ligands and steric repulsions. Usually, it has been assumed that π -acidity decreases in the order $PR_3 > SCN > NCS$. The *trans* influence of the ligands decreases in the order $PR_3 > SCN > NCS$ according to X-ray data [14, 37]. Also the *trans* influence increases in importance from the first to the third row of the transition series [18]. 5) Non polar solvents should favor the *trans* S-bonded complexes. 6) Packing factors and internal bond energies should be dominant in the solid state.

Collectively, these considerations suggest the following conclusions. For the nickel complexes, electronic effects are much more important than steric effects and consequently the "hard" nickel atom will bond to the nitrogen end of thiocyanate. When steric effects become large, the gross geometry or coordination number will change but not the thiocyanate bonding mode. For platinum complexes, where the geometry is constrained to be square planar, steric effects are perhaps slightly more important than electronic effects and platinum will bond to the sulfur end of the thiocyanate ion, unless steric effects force N-bonding to occur. Palladium is schizophrenic and steric and electronic effects are finely balanced for this metal. There seems to be no intrinsic preference for N-bonding or S-bonding and subtle changes in either steric or electronic effects will tip the balance and determine the thiocyanate bonding mode as well as geometry in any individual case.

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References

- 1 Throughout the paper "metal thiocyanate" bonding is represented as $M(SCN)$, metal isothiocyanate bonding as $M(NCS)$ and when no specific bonding mode is implied the representation $M(CNS)$ is used. The term "mixed-linkage isomers" is used to imply the presence of two thiocyanate groups coordinated in monodentate fashion but differing in their point of attachment to the metal.
- 2 a) University of Nevada, b) Iowa State University.
- 3 A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, **24**, 69 (1970).
- 4 A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, **17**, 231 (1975).
- 5 J. L. Burmeister in "The Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives", A. A. Newman Ed., Academic Press, London (1975) pp. 89ff.
- 6 G. J. Palenik, W. L. Steffen, M. Mathew, M. Li and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, **10**, 125 (1974).
- 7 J. E. Huheey and S. O. Grim, *Inorg. Nucl. Chem. Lett.*, **10**, 973 (1974).
- 8 G. J. Palenik, M. Mathew, W. L. Stephen and G. Beran, *J. Am. Chem. Soc.*, **97**, 1059 (1975).
- 9 Y. S. Wong, S. Jacobson, P. C. Chieh and A. J. Carty, *Inorg. Chem.*, **13**, 284 (1974).
- 10 A. J. Carty and S. E. Jacobson, *Chem. Comm.*, 175 (1975).
- 11 E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, **91**, 5761 (1969).
- 12 S. J. Anderson, P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. Dalton*, 1959 (1976).
- 13 A. J. Carty, P. C. Chieh, N. J. Taylor and Y. S. Wong, *J. Chem. Soc. Dalton*, 572 (1976).
- 14 G. Beran, A. J. Carty, P. C. Chieh and H. A. Patel, *J. Chem. Soc. Dalton*, 488 (1973).
- 15 A. J. Carty, *Inorg. Chem.*, **6**, 1956 (1976).
- 16 F. Basolo, W. H. Baddley and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964).
- 17 C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).
- 18 R. G. Pearson, *Inorg. Chem.*, **12**, 1712 (1973).
- 19 "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", C. A. McAuliffe, Ed., Halsted Press, New York, N.Y. (1973).
- 20 A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, **14**, 1501 (1975).
- 21 L. M. Knight and J. H. Nelson, *Inorg. Chem.*, **16**, 1307 (1977) and references contained therein.
- 22 J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273, 4300 (1952); 525 (1956).
- 23 Ni, R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **4**, 1701 (1965); Pd, S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, **4**, 56 (1970); Pt, R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 2018 (1957).
- 24 D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).
- 25 S. Fronaeus and R. Larsen, *Acta Chem. Scan.*, **16**, 1447 (1962); A. Tramer, *J. Chim. Phys.*, **59**, 232, 241, 637 (1962); C. Pecile, *Inorg. Chem.*, **5**, 210 (1966); R. A. Bailey, T. W. Michelsen and W. N. Mills, *J. Inorg. Nucl. Chem.*, **33**, 3206 (1971); R. A. Bailey, S. L. Kozak, T.

- W. Michelsen and W. N. Mills, *Coordin. Chem. Rev.*, **6**, 407 (1971).
- 26 W. J. Rohrbaugh and R. A. Jacobson, *Inorg. Chem.*, **13**, 2535 (1974).
- 27 S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2124 (1968).
- 28 W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program", U.S. Atomic Energy Commission Report, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1962).
- 29 C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL", U.S. Atomic Energy Commission Report IS-2625, Iowa State University and Institute for Atomic Research, Ames, Iowa (1971).
- 30 H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1960).
- 31 D. H. Templeton in "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England (1962) pp. 215–216, Table 3.3.2c.
- 32 W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program", U.S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1964).
- 33 C. A. Johnson, "ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", U.S. Atomic Energy Commission Report ORNL-3794 (2nd Revision with Supplemental Instructions), Oak Ridge National Laboratory, Oak Ridge, Tenn. (1970). The drawing depicts 50% probability ellipsoids.
- 34 A. W. Verstuyft, J. H. Nelson and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **12**, 53 (1976).
- 35 J. G. Verkade, *Coordin. Chem. Rev.*, **9**, 1 (1972/73).
- 36 W. McFarlane, *Quart. Rev.*, **23**, 187 (1969); S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, **6**, 133 (1967); A. Pidcock, R. E. Richards and L. M. Venzani, *J. Chem. Soc. A*, 1707 (1966) and 1970 (1968).
- 37 G. R. Clark, G. J. Palenik and D. W. Meek, *J. Am. Chem. Soc.*, **92**, 1077 (1970); G. R. Clark and G. J. Palenik, *Inorg. Chem.*, **9**, 2754 (1970).