

Infrared Studies on the Thiocyanate Ion and its Complexes with Palladium(II)

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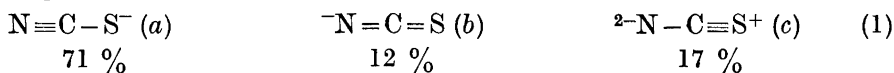
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The frequencies and the integrated absorption intensities for the stretching vibrations of the thiocyanate group in NaSCN and various mixed thiocyanato complexes of palladium(II) have been measured. A normal coordinate analysis of these vibrations has been carried out for the thiocyanate ion in order to relate the measured intensities to dipole moment changes with a stretching of an individual bond. The high values of $\partial\mu/\partial r$ indicate a large contribution from the "delocalization moment".

The spectral data have been used to distinguish between the bond types Pd-SCN and Pd-NCS. The dependence of the bonding on the nature of the other ligands in the mixed complexes is discussed.

It has been known for many years that infrared spectroscopy presents a good method for determination of the mode of bonding between a metal ion and the thiocyanate ion. The linear triatomic ion SCN^- has four normal vibrations, of which two are degenerated. They are all infrared active. On coordination, all these shift frequencies and the shifts are characteristic of the mode of bonding. The vibrations may be described approximately as a C-N stretch (ν_{CN}), a C-S stretch (ν_{CS}), and a S-C-N bend (δ_{SCN}). Their frequencies are found in the following ranges: ν_{CN} 1950-2120 cm^{-1} (generally above the value of the "free" thiocyanate ion, 2060-2070 cm^{-1} , but below 2100 cm^{-1}), ν_{CS} 760-880 cm^{-1} , δ_{SCN} 450-490 cm^{-1} for the N-bonded group and ν_{CN} 2080-2130 cm^{-1} , ν_{CS} 690-720 cm^{-1} , δ_{SCN} 400-440 cm^{-1} for the S-bonded group. As may be seen there is often an overlap of the ν_{CN} for the two types of bonding.

The behaviour of all but one of the frequencies can easily be explained by regarding how the contributions of the three resonance structures¹



would be changed upon coordination.^{2,3} The only unexpected frequency shift is towards higher frequencies usually shown by the C-N stretch in N-bonded

complexes. This fact is commented upon elsewhere³ with reference to the work of Porai-Koshits *et al.*⁴ However, ν_{CN} values also well below that of the "free" thiocyanate ion have been reported, namely 1963–1980 cm^{-1} for HNCS^{5,6} and around 1990–1980 cm^{-1} for the N-bonded hexathiocyanates of Zr(IV), Hf(IV)⁷ and Nb(V), Ta(V).⁸ In these cases it is probable that the electron redistribution effect, caused by a high covalency, is great enough to cancel out the positive frequency shift predicted from the model of Porai-Koshits *et al.*⁴ *i.e.* one with little or no change in the force constants of the C–N and C–S bonds for the N-coordinated thiocyanate ion relative to that for the "free" ion.

Besides the frequency shifts, the intensity of the C–N stretching vibration has been developed as a criterion of the bonding type.^{2,9–11} The intensity criterion says, roughly, that the integrated absorptions for the N-bonded complexes are larger and for the S-bonded ones smaller than the same quantity for the "free" thiocyanate ion. The technique was first limited to compounds which can be dissolved in a suitable solvent without dissociation or formation of mixed complexes. Later, the procedure was extended to solid samples³ and it was found that the solid state technique (KBr-disks), in spite of some loss of accuracy, could also be used to distinguish between N- and S-bonded thiocyanato complexes. Bailey *et al.*¹² have recently reported successful measurements on the solid state intensities with a somewhat modified method.

It was found¹³ that metals of class a (as classified by Ahrlund, Chatt and Davis¹⁴) generally are bonded to the thiocyanate ion *via* the nitrogen atom, whereas class b metals are bonded *via* the sulphur atom. However, Turco and Pecile¹⁵ found that in mixed complexes of such typical b-metals as palladium(II) and platinum(II) the mode of bonding depends upon the nature of the other ligands present. They suggested that the M–SCN bond usually is the most stable with these metals because of the π -bonding contribution caused by a back donation of electrons from the filled nonbonding *d*-orbitals of the metal to vacant orbitals located on the sulphur atom of the thiocyanate ion. But when strong π -acceptors, as for example tri-substituted phosphines, are introduced into the complex, the π -bonding contribution to the M–SCN bond is reduced and in such a case a M–NCS bond may become energetically more favourable. As a consequence of this one would expect a critical value in the π -acceptor strength for which the energy difference between the S- and N-bonded isomers is small enough to permit isolation of both isomers by an adjustment of the conditions of preparation. Subsequently, Burmeister and Basolo^{16,17} could prepare the first thiocyanate linkage isomers $\text{Pd}[\text{As}(\text{C}_6\text{H}_5)_3]_2(\text{NCS})_2 - \text{Pd}[\text{As}(\text{C}_6\text{H}_5)_3]_2(\text{SCN})_2$ and $\text{Pd}(\text{bipy})(\text{NCS})_2 - \text{Pd}(\text{bipy})(\text{SCN})_2$.

Because of the frequent overlap of ν_{CN} for the N- and S-bonded thiocyanate groups in these complexes, the type of bonding is usually determined on the basis of the position of ν_{CS} and δ_{SCN} ^{7–19} but also some examples of the application of the intensity criterion are available.^{3,11,20}

In a previous paper³ was discussed how the increase and decrease of the intensity of the C–N stretching vibration for the N- and S-bonded species, respectively, as compared with the "free" ligand, could be rationalized from a simple valence bond picture, using a fixed charge model. Attention was also drawn to a breakdown of the simple model when there is a large redistribu-

tion of the electron cloud upon coordination (strongly covalent bonding). In this work, the intensity measurements have been extended to the C–S stretching region as this vibration seems to be more readily influenced by the degree of interaction between metal and the thiocyanate ion than the C–N stretching vibration.

EXPERIMENTAL

Preparation of the complexes. Palladium(II) complexes of the general formula PdL_2X_2 and PdLX_2 , where X is NCS or SCN and L various mono- or bidentate organic ligands, have been prepared. The following ligands are used: Triphenylphosphine (Ph_3P), triisopropylphosphine [(i-Pr) $_3\text{P}$], tributylphosphine [(n-Bu) $_3\text{P}$], triphenylarsine (Ph_3As), triphenylstibine (Ph_3Sb), pyridine (py), 4-nitropyridine, 4-cyanopyridine, 4-benzoylpyridine, methyl isonicotinate (i-nicotin), 4-acetylpyridine (4-Acpy), isonicotinaldehyde or pyridine-4-aldehyde (4-CHOpy), 4-benzylpyridine, γ -picoline or 4-methylpyridine (4-Mepy), 4-aminopyridine, 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (4,4'-dimethylbipy), 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (5-nitrophen), 5,6-dimethyl-1,10-phenanthroline (5,6-dimethylphen), thiourea (tu), and ethylenethiourea (etu). All these ligands except 4-nitropyridine are commercially available. 4-nitropyridine was prepared from 4-nitropyridine-1-oxide according to the procedure described by Ochiai.²¹

The complexes were prepared by mixing alcoholic solutions of 1 mmol of $\text{Na}_2\text{Pd}(\text{SCN})_4$ and the stoichiometric quantity of ligand. Mostly, the complexes precipitated immediately but in some cases stirring for a period of time was necessary. Then they were filtered, washed with alcohol and ether and dried *in vacuo* over phosphorus pentoxide. All chemicals used were of analytical grade. The preparation of the linkage isomers $\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2$ and $\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2$ has been described before.³ Carbon, hydrogen, and nitrogen analyses were performed on the samples by the Division of Analytical Chemistry, Chemical Center, Lund, and some examples are given in Table 1.

Table 1. The analytical data (%) for some of the palladium(II) complexes.

Compound	Calculated			Found		
	C	H	N	C	H	N
$\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2$	61.1	4.05	3.75	60.9	4.06	3.7
$\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2$	54.7	3.62	3.36	54.3	3.68	2.7
$\text{Pd}(\text{bipy})(\text{NCS})_2$	38.0	2.13	14.79	37.5	2.22	14.4
$\text{Pd}(4,4'\text{-dimethylbipy})(\text{NCS})(\text{SCN})$	41.3	2.97	13.78	41.6	2.95	13.9
$\text{Pd}(\text{phen})(\text{SCN})_2$	41.8	2.00	13.91	42.9	2.45	13.4
$\text{Pd}(4\text{-cyanopy})_2(\text{SCN})_2$	39.0	1.87	19.50	38.2	2.04	19.9
$\text{Pd}(\gamma\text{-pic})(\text{SCN})_2$	41.2	3.45	13.71	40.8	3.51	13.8
$\text{Pd}(\text{tu})_2(\text{SCN})_2$	12.8	2.15	22.43	13.3	2.29	22.5

Recording of spectra. The infrared spectra of the samples in KBr disks were recorded on Perkin-Elmer Models 521 and 180 grating spectrophotometers. The accuracy of the frequency readings is ± 0.5 and ± 0.25 cm^{-1} and of the transmittance ± 0.5 and ± 0.4 %, respectively, according to the performance specifications of the instruments. The scale on the wavenumber axis was expanded 10 times, that is 10 and 5 cm^{-1} per 1 cm of chart paper in the ν_{CN} and ν_{CS} range, respectively. From the spectra both frequencies (ν) and the integrated absorptions (A) of the bands could be determined.

A is defined as

$$A = \frac{1}{cd} \int \ln \left(\frac{I_0}{I} \right)_{\nu} d\nu$$

where c = concentration, d = thickness of sample, ν = frequency, $I_0(I)$ = the true intensity of the incident (transmitted) radiation of frequency ν . Ramsay²² has shown that if the bands could be described by Lorentz functions $A = (K/cd) \ln (T_0/T) \nu_{\max}^a \times \Delta\nu_{1/2}^a$. Here T_0 and T are the apparent intensities of the incident and transmitted light at finite slit widths, respectively, and $\Delta\nu_{1/2}^a$ is the apparent half-band width. K is a correction factor related to the ratio of the slit width to the apparent half-band width. By using Ramsay's tables of K -values and the spectral slit width of the spectrophotometer, one can easily determine the integrated absorption (Ramsay's method of direct integration). Normally for small ratios slit width/half-band width, K is approximately $\pi/2$ and $A = (\pi/2) (\ln 10) \epsilon_{\max} \times \Delta\nu_{1/2}$ where ϵ_{\max} is the molar absorptivity as defined by $\epsilon_{\max} = (1/cd) \log (T_0/T) \nu_{\max}$. Unfortunately, the shapes of the ν_{CN} and ν_{CS} bands in the solid thiocyanate complexes were in most cases not true Lorentzian. In addition to the fact that the method of Ramsay is derived for liquids and solutions, this made us determine the integrated absorption by direct graphical integration. The spectra were run with linear absorbance and the areas under the curves were measured with a planimeter. The spectral slit width (resolution) of the spectrophotometer was about 1.5 cm^{-1} . The values of the integrated absorption determined by graphical integration were generally smaller than those obtained from Ramsay's method.

The assignment of bands due to the thiocyanate group was made by comparing the spectra of the thiocyanates with the spectra of the corresponding chloro compounds. The concentration of the solid sample in a KBr disk was obtained by accurate weighing of the sample before it was mixed with potassium bromide and by determination of the volume of the disk when it had been pressed. Every compound was examined in about ten disks with varying compositions and from the recorded spectra the accuracy of the integrated absorption (given in Table 2) was estimated to be within 10 %.

In addition to frequencies from infrared spectra also some Raman values are included in Table 2. These were obtained with the new commercial Laser-Raman spectrophotometers Cary Model 82 and Spex Ramalog.

CALCULATIONS ON THE SCN⁻ ION

The method of normal coordinate analysis. The intensities of bands arising from the fundamental vibrations are proportional to the square of the dipole derivative with respect to the Q_i normal coordinate. If A_i is the integrated absorption in $\text{M}^{-1} \text{ cm}^{-2}$ the proportionality is given by²³

$$A_i = \frac{N\pi}{3c^2 \times 10^3} \times \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \quad (2)$$

Here N is Avogadro's number, c the velocity of light in cm/s and μ the total dipole moment of the molecule in esu cm.* Hence, the absolute value of $\partial \mu / \partial Q_i$ could be obtained from experimental determinations of the integrated absorption:

$$\left| \frac{\partial \mu}{\partial Q_i} \right| = \left(\frac{3c^2 \times 10^3 A_i}{N\pi} \right)^{\frac{1}{2}} (\text{esu g}^{-\frac{1}{2}}) \quad (3)$$

Eqn. (2) is derived for isolated molecules in the gas phase and when handling solid samples one must consider changes in the vibrational intensities caused

* For the sake of convenient comparison with existing data the CGS system has been used in the derivations and the integrated absorption is expressed in $\text{M}^{-1} \text{ cm}^{-2}$. The SI unit for the integrated absorption would be m mol^{-1} , for the velocity of light m s^{-1} and for the dipole moment C m. In this case eqn. (2) becomes $A_i = 8.988 \times 10^6 \frac{N\pi}{3c^2} \left(\frac{\partial \mu}{\partial Q_i} \right)^2$.

Table 2. Spectral data of the investigated complexes. The values of ϵ , $\epsilon \times \Delta\nu_{1/2}$, and A are calculated per SCN group.

Compound	ν_{CN} (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	$\Delta\nu_{1/2}$ (cm^{-1})	$\epsilon \times \Delta\nu_{1/2}$ $\times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-2}$)	A_{CN} $\times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-2}$)	ν_{CS} (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	$\Delta\nu_{1/2}$ (cm^{-1})	$\epsilon \times \Delta\nu_{1/2}$ ($\text{M}^{-1}\text{cm}^{-2}$)	A_{CS} ($\text{M}^{-1}\text{cm}^{-2}$)	δ_{SCN} (cm^{-1})
A NaSCN	2070	310	39	1.22	3.25	755	6	10	60	150	{484 470}
B Pd(PPh ₃) ₂ (NCS) ₂	2092	720	24.5	1.76	5.76	{851 846sh}	(70)	(13)	(900)	2200	
C Pd[P(i-Pr) ₃] ₂ (NCS) ₂	2106	900	23	2.07	6.05	848	130	6	780	2600	
D Pd[P(n-Bu) ₃] ₂ (NCS) ₂	2105	990	23	2.28	6.70	847	120	9	1080	3100	448
E Pd(AsPh ₃) ₂ (NCS) ₂	2088	720	27	1.94	6.03	853	100	10	1000	2250	
F Pd(4-nitropy) ₂ (NCS) ₂	2109	700	29	2.03	5.96	^a	^a	^a	^a	^a	455 ^b
G Pd(bipy)(NCS) ₂	2099	700	32	2.24	5.62	{843 849sh}	(38)	(9)	(340)	990	458
H Pd(5-nitrophen)(NCS)- (SCN)	2090	340	46	1.58	4.13	^a	^a	^a	^a	^a	457
I Pd(4,4'-dimethylbipy)- (NCS)(SCN)	2120	290	15	0.44	1.09	692	4	7	28	64	{424 419
J Pd(AsPh ₃) ₂ (SCN) ₂	2099	610	36	2.18	6.17	839 ^b	58 ^b	9 ^b	522 ^b	1014 ^b	455
K Pd(SbPh ₃) ₂ (SCN) ₂	2121	310	11	0.34	0.84	702	4.5	9	41	121	^a
L Pd(phen)(SCN) ₂	2119	350	8	0.28	0.87	^a	^a	^a	^a	^a	417
M Pd(5,6-dimethylphen)- (SCN) ₂	2093	720	11	0.79	2.80	^a	^a	^a	^a	^a	
	2116	400	9	0.36	1.12	695	3.5	7	25	60	418
	{2112 2106}	{490 490}	{7 7}	{0.34 0.34}	2.11	698	3.5	7	25	70	420

Table 2. Continued.

N	Pd(4-cyanopy) ₂ (SCN) ₂	2113	470	10	0.47	1.35	{701 696	10 11	3 4	30 44	265	419
	Raman	2119					{702 699					
O	Pd(4-benzoylpy) ₂ (SCN) ₂	2119	370	7	0.26	0.95	^a	^a	^a	^a	^a	
P	Pd(i-nicotin) ₂ (SCN) ₂	2117	350	9	0.31	1.04	^a	^a	^a	^a	^a	424
Q	Pd(4-Aepy) ₂ (SCN) ₂	2120	350	12	0.42	1.30	706	6	10	60	134	
R	Pd(4-CHOpy) ₂ (SCN) ₂	2117	250	24	0.60	1.41	697	3	9	27	62	
S	Pd(py) ₂ (SCN) ₂	{2114 2102sh	{300 (300)	{9 (9)	{0.27 (0.27)	1.67	^a	^a	^a	^a	^a	426
T	Pd(4-benzylpy) ₂ (SCN) ₂	2117	320	7	0.22	0.83	702	9	3	27	71	
U	Pd(4-Mepy) ₂ (SCN) ₂	2110	280	10	0.28	0.91	698	3	6	18	50	
V	Pd(4-aminopy) ₂ (SCN) ₂	2116	580	14	0.81	2.40	716	4	8	32	106	
W	Pd(tu) ₂ (SCN) ₂	2110	740	12	0.89	2.90	{714 704	7 11	50 41	350 450	2370	
	Raman	2110					{716 704					
X	Pd(etu) ₂ (SCN) ₂	2103	310	13	0.40	1.61	703	4	7	28	90	
Y	K ₂ Pd(SCN) ₄	{2094 2124	{140 190	{12 8	{0.17 0.15}	0.97	{704 698sh	{4 (5)	{7 (7)	{28 (35)	120	

^a Band masked by the absorption of the organic ligand. ^b The values are uncertain because of a large absorption of the organic ligand in that region. Abbreviations: For the abbreviations in the formulae of the compounds see text below "EXPERIMENTAL"; sh means shoulder.

by intermolecular interactions and also the dependency of the intensity on the refractive index of the phase.²⁴ Ratajczak and Orville-Thomas²⁵ have derived a general formula which applies to molecules in any phase. However, the results of Yamada and Person²⁶ in their studies of the infrared intensities in the solid phase of linear triatomic molecules indicate that the intensities of the stretching vibrations of, *e.g.*, a thiocyanate group in the solid phase probably would not differ drastically from those in the gas phase and therefore eqn. (2) would be a good approximation in this case.

Since all atoms in the molecule move in phase for each fundamental vibration the normal coordinates are complicated functions of changes in bond lengths and bond angles. It is desirable from a chemical point of view to relate the change of dipole moment to the individual bonds. This could be done by carrying out a normal coordinate analysis which is based on accurate knowledge of the potential and kinetic energy of the system. Reviews of the method of normal coordinate calculations and the nomenclature used can be found in Refs. 27 and 28. In the following a calculation of the change of dipole moment with the bond lengths in the "free" thiocyanate group will be made in a manner similar to the procedure of Robinson²⁹ and Orville-Thomas *et al.*^{30,31}

The normal coordinates Q_i (in terms of a column matrix Q) are related to the symmetry coordinates S_i (S) by a transformation

$$S = LQ \text{ or } Q = L^{-1}S \quad (4)$$

where L^{-1} is the inverse of matrix L . The linear NCS group belongs to the point group $C_{\infty v}$. That means that the two stretching vibrations and the doubly degenerate bending vibration are in different symmetry classes (Σ^+ and Π , respectively) and therefore they can be treated separately. For the two stretching vibrations (4) can be written

$$Q_i = L_{i1}^{-1}S_1 + L_{i2}^{-1}S_2 \quad (i = 1, 2)$$

As the stretching vibrations imply changes only in the interatomic distances, a relevant connection between the symmetry and the internal coordinates is $S_1 = \Delta r_1 = \Delta r_{NC}$ and $S_2 = \Delta r_2 = \Delta r_{CS}$. Thus

$$Q_i = L_{i1}^{-1} \Delta r_1 + L_{i2}^{-1} \Delta r_2 \quad (i = 1, 2) \quad (5)$$

Using the GF matrix technique of Wilson^{27,32} the vibrational problem leads to a secular equation which symbolically can be written as $|GF - E\lambda| = 0$. Here both F and G are symmetrical matrices. The components of F are the force constants $F = \begin{pmatrix} f_1 & f_{12} \\ f_{12} & f_2 \end{pmatrix}$ where f_1 and f_2 are the force constants of the N-C and C-S bonds, respectively, and f_{12} is the bond-bond interaction constant. The elements of the G matrix can easily be shown to be (see Ref. 27 SEC. 4-2)

$$G = \begin{pmatrix} \mu_N + \mu_C & -\mu_C \\ -\mu_N & \mu_C + \mu_S \end{pmatrix}$$

where μ is the reciprocal mass. The homogeneous equations for the amplitudes (L^{-1}) for this form of the secular equation are (eqn. 42 in Ref. 32)

$$[(GF)_{11} - \delta_{11}\lambda_m]L_{m1}^{-1} + [(GF)_{21} - \delta_{21}\lambda_m]L_{m2}^{-1} = 0$$

where $l, m = 1$ or 2 and δ_{kl} , the Kronecker delta symbol, is unity if $k = l$ and is zero otherwise. λ is determined from the observed wave numbers of the two stretching vibrations by $\lambda = 4\pi^2c^2\bar{\nu}^2$.

These homogeneous equations give only the ratios of the components of L^{-1} . Thus for $l = 1$

$$\frac{L_{m2}^{-1}}{L_{m1}^{-1}} = - \frac{(GF)_{11} - \lambda_m}{(GF)_{21}} \quad (6)$$

$(GF)_{11}$ and $(GF)_{21}$ are elements of a matrix GF. That is, in this case,

$$(GF)_{11} = (\mu_N + \mu_C)f_1 - \mu_C f_{12} \quad (7a)$$

$$(GF)_{21} = -\mu_C f_1 + (\mu_C + \mu_S)f_{12} \quad (7b)$$

The separate values of the elements of L^{-1} can be obtained by the normalization condition. This may be written³² as $L^{-1}G(L')^{-1} = E$ where L' is the transpose of L and E is the unit matrix. If $(L_0^{-1})_{mk}$ is the unnormalized value of $(L^{-1})_{mk}$ and K_m the normalizing constant then

$$K_m = \left[\sum_{k,l=1}^2 (L_0^{-1})_{mk} (L_0^{-1})_{ml} G_{kl} \right]^{-\frac{1}{2}}$$

If for example $(L_0^{-1})_{m1}$ taken equal to unity then

$$K_m = [G_{11} + 2(L_0^{-1})_{m2} G_{12} + (L_0^{-1})_{m2}^2 G_{22}]^{-\frac{1}{2}} \quad (8)$$

The knowledge of the ratio L_{m2}^{-1}/L_{m1}^{-1} now directly gives the separate normalized values of L^{-1} .

The dipole derivative with respect to the changes in bond lengths $\partial\mu/\partial r_k$ can be written as

$$\frac{\partial\mu}{\partial r_k} = \left(\frac{\partial\mu}{\partial Q_1} \right) \left(\frac{\partial Q_1}{\partial r_k} \right) + \left(\frac{\partial\mu}{\partial Q_2} \right) \left(\frac{\partial Q_2}{\partial r_k} \right) \quad (9)$$

From eqn. (5) is obtained

$$\frac{\partial Q_i}{\partial r_k} = L_{ik}^{-1}$$

which on substitution in eqn. (8) gives

$$\frac{\partial\mu}{\partial r_1} = L_{11}^{-1} \frac{\partial\mu}{\partial Q_1} + L_{21}^{-1} \frac{\partial\mu}{\partial Q_2} \quad (10a)$$

$$\frac{\partial\mu}{\partial r_2} = L_{12}^{-1} \frac{\partial\mu}{\partial Q_1} + L_{22}^{-1} \frac{\partial\mu}{\partial Q_2} \quad (10b)$$

Results. The wave numbers and the integrated absorptions of the two stretching vibrations of the "free" thiocyanate ion (NaSCN) used in the calculations can be found in Table 2. The force constants have previously been determined by Jones¹ ($f_1 = 15.95 \times 10^5$, $f_2 = 5.18 \times 10^5$ and $f_{12} = 0.9 \times 10^5$ dyn/cm).

This leads to the following L^{-1} matrix elements

$$\begin{array}{lll} L_{11}^{-1} = \pm 3.088 \times 10^{-12} & L_{12}^{-1} = \mp 0.335 \times 10^{-12} & (g^{\ddagger}) \\ L_{21}^{-1} = \pm 2.898 \times 10^{-12} & L_{22}^{-1} = \pm 4.866 \times 10^{-12} & (g^{\ddagger}) \end{array}$$

With these values inserted in eqns. 10 a and b together with the $\partial\mu/\partial Q_i$'s from eqn. 3 the absolute values of the dipole derivative can be derived. Since the sign of the $\partial\mu/\partial Q_i$ is not known, the values of $\partial\mu/\partial r_i$ will be dependent on the sign combination chosen.

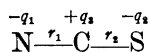
$$\begin{array}{l} \left| \frac{\partial\mu}{\partial r_1} \right| = 1.30 \text{ a.u. (different signs for } \partial\mu/\partial Q_i) \text{ or} \\ \left| \frac{\partial\mu}{\partial r_1} \right| = 1.48 \text{ a.u. (similar signs for } \partial\mu/\partial Q_i) \\ \left| \frac{\partial\mu}{\partial r_2} \right| = 0.30 \text{ a.u. (different signs for } \partial\mu/\partial Q_i) \text{ or} \\ \left| \frac{\partial\mu}{\partial r_2} \right| = 0.002 \text{ a.u. (similar signs for } \partial\mu/\partial Q_i) \end{array}$$

As will be discussed later, the values obtained for similar signs for $\partial\mu/\partial Q_i$ can definitely be excluded.

The dipole moment of a molecule, symbolized μ , is defined as the distance between the centres of positive and negative charge, multiplied by the size of one of them. For an ion, *e.g.* NCS^- , with a total negative charge, this charge would not contribute to the dipole moment or the change of dipole moment in a vibration as it all the time is situated in the centre of negative charge. The total dipole moment could be written as a sum of the bond moments

$$\mu = \mu_1 + \mu_2$$

and if the charge distribution is (when leaving the negative unit charge out of account)



the dipole moment is $\mu = q_2 r_2 - q_1 r_1$ ($q_1 + q_2 = q_3$). When this relation is derived (a) with respect to r_1 keeping r_2 constant, (b) with respect to r_2 keeping r_1 constant one gets

$$\frac{\partial\mu}{\partial r_1} = r_2 \frac{\partial q_2}{\partial r_1} - q_1 - r_1 \frac{\partial q_1}{\partial r_1} = -q_1 - M_1 \quad (11a)$$

$$\frac{\partial\mu}{\partial r_2} = q_2 + r_2 \frac{\partial q_2}{\partial r_2} - r_1 \frac{\partial q_1}{\partial r_2} = q_2 + M_2 \quad (11b)$$

M_1 and M_2 would correspond to the "delocalization moment" of Person and Hall³³ and is a measure of the contribution to the dipole moment change from the movements of delocalized electrons of the vibrating thiocyanate ion.

The charge distribution in the thiocyanate ion has been calculated by Di Sipio *et al.*³⁴ Their charges on the sulphur and nitrogen atoms are $q_S = -0.48$ and $q_N = -0.51$, which are in good agreement with the values expected from the resonance structures (1). However, other calculations³⁵ indicate more negative values, at least for sulphur, and so does an estimation made by Folkesson.³⁶ Using the ESCA technique, he measured the N1s and S2p electron binding energies of NaSCN. Then, from a correlation of binding energies of

other N and S containing substances and corresponding MO SCF calculated charges (*cf.*, *e.g.*, Ref. 37), he could obtain the values $q_S = -0.72$ and $q_N = -0.70$ a.u. As has been mentioned above, the negative unit charge of the thiocyanate ion does not effect the dipole moment and could be placed in the negative charge centre. Jones¹ has determined the bond distances to be $r_{CN} = 1.17$ Å and $r_{CS} = 1.61$ Å and therefore the negative charge centre is situated somewhere between the carbon and the sulphur. If the values of Folkesson are used, the effective charges would be $q_1, q_2 \approx 0.21$ a.u. When the values of q_1 and q_2 are inserted in eqns. 11a and b together with the $\partial\mu/\partial r_i$'s two different cases appear: Ratio $\partial\mu/\partial Q_i$ negative: $M_1 = 1.09$ a.u., $M_2 = 0.09$ a.u.; positive: $M_1 = 1.27$ a.u., $M_2 = -0.21$ a.u.

In the valence bond description the "delocalization moment" is connected with the changes in the relative weights of the resonance hybrids (1) of the thiocyanate ion during the vibration. A stretching of a bond tends to favour the structure in which that bond is single and it is obvious that this effect works in the same direction upon the change of the dipole moment as the stretching of a bond in a fixed charge model would do. Therefore, a negative value of M is unacceptable and makes it possible to exclude the $\partial\mu/\partial r_i$ values for similar signs for $\partial\mu/\partial Q_i$.

The contribution from the "delocalization moment" is very large, especially for the C-N stretching vibration. The value of $\partial\mu/\partial r_{CN}$ expected from a fixed charge model would be 0.21 a.u., that is only one sixth of the value calculated from the integrated absorption experimentally determined. Therefore, it seems obvious that such a model is insufficient when treating molecules of this kind and that the possibility of delocalized charges must be considered in understanding infrared intensities.

RESULTS OF THE MEASUREMENTS ON THE Pd-COMPLEXES

In Table 2 all the spectral data of the bands assigned to the C-N and C-S stretching vibrations of the thiocyanate group are listed for the complexes investigated. In some special cases the frequency of the bending vibration is included. The type of bonding is determined mostly on the basis of the integrated absorption of the C-N vibration (A_{CN}) and the C-S frequency (ν_{CS}). When the latter is questionable or when the band is masked by the absorption of the other ligand present, also the NCS bending frequency is used as a supporting criterion. Thus the compounds **B-G** are believed to be fully N-bonded and compounds **J-Y** S-bonded.

All compounds listed in Table 2 are probably square-planar with *trans* configuration¹⁷ except, of course, those containing a bidentate ligand, such as compounds **G, H, I, L, and M**, in which the two thiocyanate groups necessarily must be *cis* to each other. In such *cis* compounds both the in-phase and out-of-phase vibrational modes associated with the C-N (C-S) stretching of the two thiocyanate groups are infrared active, whereas in the *trans* compounds only the out-of-phase one is infrared active. Thus, one should expect a splitting of the absorption bands in the *cis* compounds. As seen in Table 2 there is a splitting of the C-N frequency for compounds **H, I and M** (see

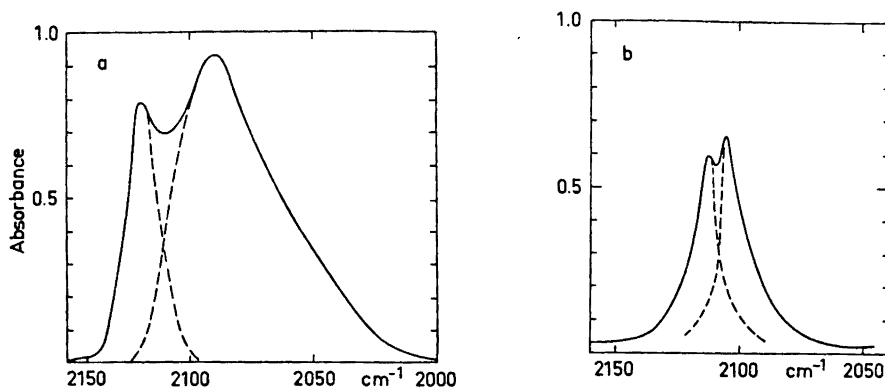


Fig. 1. Spectra of (a) Pd(5-nitrophen)(NCS)(SCN), (b) Pd(5,6-dimethylphen)(SCN)₂.

also Fig. 1), but for **G** and **L** only a single band is observed, possibly owing to accidental degeneracy. Contrary to the case in compound **M** (Fig. 1b), the two absorption bands in the C–N stretching range of the compounds **H** (Fig. 1a) and **I** showed very different shapes, one having integrated absorption as a N-bonded thiocyanate group, the other as a S-bonded group. Moreover, the existence of bands both in the N- and the S-bonded ranges of the C–S stretching and SCN bending vibrations, makes it plausible that in these compounds one thiocyanate group is linked *via* nitrogen and one *via* sulphur. Of course it could just as well be a mixture of PdL(NCS)₂ and PdL(SCN)₂ but, as Bertini and Sabatini¹⁹ have pointed out, one would not expect the same spectrum of a mixture when it was prepared at two widely different temperatures. We have prepared the compounds **G** and **H** at -20°C and $+25^{\circ}\text{C}$, warmed them to 130°C and used varying pressures when pressing the KBr disks, but found no difference in the spectrum. Palladium(II) complexes with mixed thiocyanate bonding in the same molecule, as compounds **H** and **I** are believed to be, are not too numerous but recently Meek *et al.*²⁰ have reported several examples of this kind when bidentate ligands are present.

Splitting is also observed for some of the complexes with *trans*-configuration. Causes of these splittings may be distortions from the regular D_{4h} symmetry brought about by, *e.g.*, non-linearity, but also, as the samples are solid, owing to site symmetry and other solid-state effects.

DISCUSSION

As mentioned in the introduction above, the transformation from the normally more stable Pd–SCN bonding to Pd–NCS bonding could be ascribed to a high π -bonding ability of the other ligands present. Thus, the π -bonding hypothesis has been used¹⁸ to explain the change from S-bonded thiocyanates for triphenylstibine to both S- and N-bonded for triphenylarsine and to N-bonded for triphenylphosphine by the order of increasing π -

capacity of the ligands. However, this order is somewhat ambiguous^{38,39} and also steric factors can promote a change of the bonding type in these systems. From theoretical considerations¹³ one would expect a M–SCN complex to be bent whilst a M–NCS complex could be either linear or bent. Not very many structural studies on N-bonded thiocyanato complexes of palladium(II) have been carried out but in Pd[(C₆H₅)₂PCH₂CH₂CH₂N(CH₃)₂](SCN)(NCS)⁴⁰ the angle between Pd and the NCS group is 177.6° whilst that between Pd and the SCN group is 107.3°. If the bond angles are similar in the mixed complexes mentioned above, the change from M–SCN to M–NCS bonding could as well be explained by the smaller size of phosphorus as compared with arsenic and antimony which places the phenyl groups nearer to the metal, thus producing a greater steric hindrance to an angular M–SCN arrangement than to a linear M–NCS.

Among the ligands with nitrogen as donor atom shown in Table 2, only the bidentate 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, and 5-nitro-1,10-phenanthroline and the monodentate 4-nitropyridine are able to promote N-bonded thiocyanates. 1,10-Phenanthroline itself gives S-bonded thiocyanates, but when a strongly electron-withdrawing group such as -NO₂ is substituted onto it, one of the thiocyanate groups will change its bonding mode. On the other hand, alkyl substitution (in 5,6-dimethyl-1,10-phenanthroline) would enhance the S-bonding, as it decreases the ability of the ligand to withdraw charge from the central metal atom. This electronic effect could be treated more quantitatively for the *para*-substituted pyridines.

The ability of a substituent to either withdraw electrons from an aromatic ring or donate them into it can be expressed by its Hammett constant, σ .^{41,42} Thus, a positive value of σ means that a substitution decreases the electron density of the ring and *vice versa*. Table 3 shows the effective substituent constant $\bar{\sigma}$ derived by Fischer *et al.*⁴³ for *para*-substituted pyridine systems. The $\bar{\sigma}$ values are related to the basic strength of the substituted compound (*cf.* the pK_a values of the corresponding pyridinium ions, also included in Table 3). In a series of such analogous compounds, increasing $\bar{\sigma}$ (decreasing basicity) would be related to lower electronic density on the pyridine nitrogen and, at coordination, a pronounced electron withdrawal from the central metal atom either by an inductive or π -electron accepting mechanism. Therefore, one expects that a change of substituents with increasing $\bar{\sigma}$ would cause a continuous decrease of the π -bonding contribution to the Pd–SCN bond in

Table 3. The effective Hammett substituent constants $\bar{\sigma}$ and the pK_a values of the *para*-substituted pyridines. Values are taken from Ref. 43.

Substituent	$\bar{\sigma}$	pK_a	Substituent	$\bar{\sigma}$	pK_a
4-NH ₂	-0.65	9.12	4-COCH ₃	0.28	3.51
4-CH ₃	-0.14	6.03	4-COOCH ₃	0.28	3.49
4-CH ₂ .C ₆ H ₅	-0.07	5.59	4-COC ₆ H ₅	0.31	3.35
H	0	5.21	4-CN	0.55	1.86
4-CHO	0.11	4.52	4-NO ₂	0.63	1.39

$\text{PdL}_2(\text{SCN})_2$ ($\text{L} = \textit{para}$ -substituted pyridine) and that at some point a change to $\text{PdL}_2(\text{NCS})_2$ may occur. As can be seen in Table 2, this happens when the nitro group with the largest $\bar{\sigma}$ is substituted. The effect of increasing $\bar{\sigma}$ on the complexes which remain S-bonded is illustrated in Fig. 2 with respect to their integrated absorption A_{CN} . Even if a certain amount of π -bonding is accepted

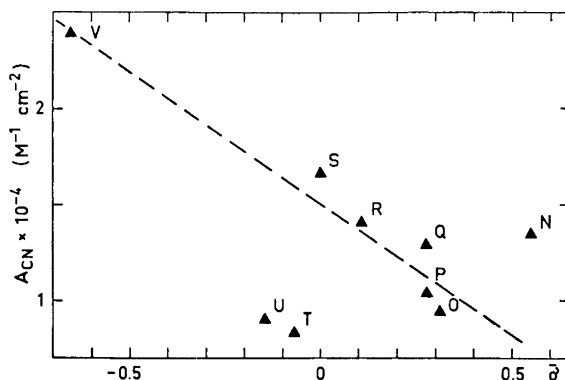


Fig. 2. The dependence of the integrated absorption A_{CN} of $\text{PdL}_2(\text{SCN})_2$ ($\text{L} = \textit{para}$ -substituted pyridine) on the effective Hammett substituent constants $\bar{\sigma}$.

in a Pd–SCN bond, it must be remembered that it for the main part is a σ bond resulting from a lone-pair donation from the sulphur atom. Such a donation would be facilitated if a strong electron-withdrawing group is introduced into the complex. From the simple valence bond picture^{2,3} using the canonical structures of Jones (1), a decrease of A_{CN} is expected when $\bar{\sigma}$ is increased. Such a decrease may also be found in Fig. 2 although it is not continuous if all the values are regarded.

Also the other complexes in Table 2 are approximately ordered in a series of falling electron-accepting ability of the organic ligand. As no definite correlation between this ability, the frequencies and the integrated absorptions within the groups of N- or S-bonded thiocyanate complexes could be found, there must be other factors than the electronic, which are important. Thus, steric requirements may cause deviations in the metal-thiocyanate bond angles from one complex to another and would change the frequencies and perhaps also the intensities of the thiocyanate group vibrations.

The change in A_{CN} upon coordination can qualitatively be explained by the aid of the resonance structures (1) of the thiocyanate ion,^{2,3} if an increase of dipole moment over the C–N bond also implies an increased value of the dipole derivate. For A_{CS} , the same procedure would predict a decrease of the “free ion” value upon coordination *via* N and an increase upon coordination *via* S. But the report of Tramer⁹ that for $\text{Hg}(\text{SCN})_4^{2-}$ in acetone solution the ratio $A_{\text{CS}}(\text{Hg}(\text{SCN})_4^{2-})/A_{\text{CS}}(\text{SCN}^-) < 1$ indicated that the prediction above would be wrong and this is confirmed by the results given in Table 2. However, the suggestion that a larger dipole moment means a larger dipole derivate

and thus integrated absorption cannot be fully true if there is a "delocalization moment" contributing to the static one. An N-coordination for example would favour the resonance structures *b* and *c* in (1), that is there would be an increase in bond order and probably a decrease of the C–S bond moment. But when the C–S bond is stretched the structure *a* where this bond is single would be promoted, and this structure has the largest C–S bond moment of all. Therefore, during the vibration (stretching) an N-coordinated thiocyanate ion would have a greater change of dipole moment over the C–S bond than the uncoordinated ion. The situation would be the reverse when there is S-coordination.

As can be seen in Table 2, $A_{\text{CN}}(\text{M}-\text{SCN})$ and $A_{\text{CS}}(\text{M}-\text{SCN})$ are generally about one half of the corresponding values of NaSCN . $A_{\text{CN}}(\text{M}-\text{NCS})$ is twice the $A_{\text{CN}}(\text{SCN}^-)$ but $A_{\text{CS}}(\text{M}-\text{NCS})$ is about twenty times as large as $A_{\text{CS}}(\text{SCN}^-)$. The same relationships are shown by $\text{Hg}(\text{SCN})_4^{2-}$ in acetone solution⁹ and gaseous HNCS as could be estimated from the spectra reported by Reid.⁵ The large value of the $A_{\text{CS}}(\text{M}-\text{NCS})$, which means 4.5 times larger $\partial\mu/\partial Q_i$ than for the "free" thiocyanate ion, is very interesting, but difficult to explain quantitatively at this point. But it may certainly be connected with a much more pronounced "delocalization moment" at the C–S stretching vibration for the S-bonded thiocyanate ion than for the other forms.

Generally, the differences in absorption frequencies and integrated absorption within the groups of N- and S-bonded thiocyanates are not very great but some examples of abnormal values are found, *viz.* the C–S stretching intensity of the thiourea compound **W** and that of the 4-cyanopyridine compound **N**. (The frequencies of these compounds are not remarkable and are nearly the same when determined with Raman.) This large intensity, at least for the thiourea compound, is likely to be caused by Fermi resonance. Two bands are observed in the C–S stretching region of the S-bonded thiocyanate ion but probably one of them corresponds to a C=S and N–C–N stretching of the *thiourea*. This band usually is found at about 730 cm^{-1} , but it should be lowered at coordination because of the reduced double bond character of the C=S bond. This vibration is of A_1 symmetry type⁴⁴ and so is the C–S stretching vibration of the thiocyanate group ($\Sigma^+ \equiv A_1$). Furthermore, these two vibrations probably would be of nearly the same energy. Under these conditions, Fermi resonance often produces vibrational perturbations⁴⁵ between the two vibrations which involve, besides frequency shifts, an enlargement of the absorption bands.

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REFERENCES

1. Jones, L. H. *J. Chem. Phys.* **25** (1956) 1069.
2. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1447.
3. Larsson, R. and Mieziš, A. *Acta Chem. Scand.* **23** (1969) 37.

4. Kharitonov, Yu. Ya., Tsintsadze, G. V. and Porai-Koshits, M. A. *Russ. J. Inorg. Chem.* **10** (1965) 427.
5. Reid, C. J. *Chem. Phys.* **18** (1950) 1512.
6. Barakat, T. M., Legge, N. and Pullin, A. D. E. *Trans. Faraday Soc.* **59** (1963) 1764.
7. Bailey, R. A., Michelsen, T. W. and Nobile, A. A. *J. Inorg. Nucl. Chem.* **32** (1970) 2427.
8. Knox, G. F. and Brown, T. M. *Inorg. Chem.* **8** (1969) 1401.
9. Tramer, A. *J. Chim. Phys.* **59** (1962) 232.
10. Larsson, R. and Mieziš, A. *Acta Chem. Scand.* **19** (1965) 47.
11. Pecile, C. *Inorg. Chem.* **5** (1966) 210.
12. Bailey, R. A., Michelsen, T. W. and Mills, W. N. *J. Inorg. Nucl. Chem.* **33** (1971) 3206.
13. Lewis, J., Nyholm, R. S. and Smith, P. W. *J. Chem. Soc.* **1961** 4590.
14. Ahrlund, S., Chatt, J. and Davies, N. R. *Quart. Rev. Chem. Soc.* **12** (1958) 265.
15. Turco, A. and Pecile, C. *Nature* **191** (1961) 66.
16. Basolo, F., Burmeister, J. L. and Poe, A. J. *J. Am. Chem. Soc.* **85** (1963) 1700.
17. Burmeister, J. L. and Basolo, F. *Inorg. Chem.* **3** (1964) 1587.
18. Sabatini, A. and Bertini, I. *Inorg. Chem.* **4** (1965) 1665.
19. Bertini, I. and Sabatini, A. *Inorg. Chem.* **5** (1966) 1025.
20. Meek, D. W., Nicpon, P. E. and Meek, V. I. *J. Am. Chem. Soc.* **92** (1970) 5351.
21. Ochiai, E. *J. Org. Chem.* **18** (1953) 534.
22. Ramsay, D. A. *J. Am. Chem. Soc.* **74** (1952) 72.
23. Thorndike, A. M., Wells, A. J. and Wilson, E. B. *J. Chem. Phys.* **15** (1947) 157.
24. Steele, D. *Quart. Rev. Chem. Soc.* **18** (1964) 21.
25. Ratajczak, H. and Orville-Thomas, W. J. *Trans. Faraday Soc.* **61** (1965) 2603.
26. Yamada, H. and Person, W. B. *J. Chem. Phys.* **43** (1965) 2519.
27. Wilson, E. B., Decius, J. G. and Cross, P. C. *Molecular Vibrations*, McGraw, New York 1955.
28. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York and London 1963.
29. Robinson, D. Z. *J. Chem. Phys.* **19** (1951) 881.
30. Rowland Davies, P. and Orville-Thomas, W. J. *J. Mol. Structure* **4** (1969) 163.
31. Thomas, G. A., Ladd, J. A. and Orville-Thomas, W. J. *J. Mol. Structure* **4** (1969) 179.
32. Wilson, E. B. *J. Chem. Phys.* **9** (1941) 76.
33. Person, W. B. and Hall, L. C. *Spectrochim. Acta* **20** (1964) 771.
34. DiSipio, L., Oleari, L. and deMichelis, G. *Coord. Chem. Rev.* **1** (1966) 7.
35. Karlsson, G. and Manne, R. *Phys. Scripta* **4** (1971) 119.
36. Folkesson, B. *Private communication*.
37. Folkesson, B. *Acta Chem. Scand.* **27** (1973) 287.
38. Chatt, J., Duncanson, L. A. and Venanzi, L. M. *J. Chem. Soc.* **1955** 4461.
39. Horrocks, Jr., W. D. and Craig Taylor, R. *Inorg. Chem.* **2** (1963) 723.
40. Clark, G. R. and Palenic, G. J. *Inorg. Chem.* **9** (1970) 2754.
41. Hammett, L. P. *Physical Organic Chemistry*, McGraw, New-York 1940.
42. Jaffé, H. H. *Chem. Rev.* **53** (1953) 191.
43. Fischer, A., Galloway, W. J. and Vaughan, J. J. *J. Chem. Soc.* **1964** 3591.
44. Yamaguchi, A., Penland, R. B., Mizushima, S., Lane, T. J., Curran, C. and Quagliano, J. V. *J. Am. Chem. Soc.* **80** (1958) 527.
45. Szymanski, H. A. *Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York 1964, p. 149.

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