group is required to be planar in P2/a and, within statistical significance, does not deviate from D_{3h} symmetry. The N–O distances are not significantly different from the generally accepted N–O distance of 1.22 A.[3b,26,27]

Acknowledgment.—We wish to acknowledge financial support from the National Science Foundation, Grant No. GP-1575.

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(26) R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, **10**, 567 (1957)

(27) We wish to thank one of the referees for his excellent criticism of our original choice of space group Pa. We carefully reexamined the entire problem, and, as seen above, the correct space group seems to be P2/a.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
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Infrared Spectra of Substituted Thiocyanate Complexes. The Effect of the Substituent on Bond Type. II

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Received September 7, 1965

Complexes of the general formula $[PdL_2(SCN)_2]$, where L = methyl ester of isonicotinic acid, 4-nitropyridine, or 4-cyanopyridine and L_2 = 5-methyl-*o*-phenanthroline, 5,6- and 4,7-dimethyl-*o*-phenanthroline, 5-chloro-*o*-phenanthroline, 5-methyl-6-nitro-*o*-phenanthroline, 4,7-diphenyl-*o*-phenanthroline, 5-nitro-*o*-phenanthroline, or 4,4′-dimethyl-2,2′-bipyridine, have been prepared. Their infrared spectra were used to establish the bond type Pd–S or Pd–N. The dependence of the bond type on the substituent of the organic ligand is discussed.

Introduction

The problem of which atom of the thiocyanate group is linked to the metal in thiocyanate complexes has been extensively studied by analyses of infrared spectra.[1–3]

Various authors[1,3,4] have noticed that the value of the C–S stretching frequency is diagnostic of the type of bonding: *ca.* 700 cm^{-1} for S-bonded thiocyanate compounds, 760–880 cm^{-1} for N-bonded thiocyanate complexes. Furthermore, the other vibration modes of the NCS group have been studied, and it has been concluded that, although the C–N stretching frequency does not have a shift characteristic for S- and N-bonded complexes,[1] the NCS bending frequency is still indicative of the type of bonding:[3,5] 450–490 cm^{-1} for N-bonded thiocyanates; 400–440 cm^{-1}, often with weaker bands at higher frequencies, for S-bonded thiocyanate complexes.

Turco and Pecile[4] have studied complexes in which as well as the thiocyanate group one or more organic ligands are present, and they have found that substituting two of the NCS ions in the S-bonded complexes $[Pt(SCN)_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ with two trialkylphosphines causes isomerization from M–S to M–N bonding. Subsequently, Basolo and Burmeister[6,7] have found that $[Pd(bipy)(NCS)_2]$ and $[Pd(As(C_6H_5)_3)_2(NCS)_2]$ both give linkage isomers, and they succeeded in separating them. These authors[4,6,7] have drawn these conclusions by analyzing only the values of the C–S stretching frequency.

In one of our previous papers[8] we drew attention to the fact that the assignment of the band due to C–S stretching may be incorrect, if the infrared investigation is not extended so far as the region of the NCS bending frequencies. In fact, the first harmonic of the NCS deformation frequency of an S-bonded thiocyanate compound lies in the range 820–880 cm^{-1} and can therefore be assigned to the C–S stretching, diagnostic of an N-bonded thiocyanate complex. Furthermore we drew attention to the fact that in the compounds $[PdL_2(NCS)_2]$ the C–N stretching also assumes characteristic forms and values: >2100 cm^{-1} and sharp for S-bonded thiocyanates; ≤ 2100 cm^{-1} and broad for N-bonded thiocyanates.

In this article we intend to study the effect of variously substituted organic ligands, whose donor atom is an aromatic nitrogen, on the type of bonding of the thiocyanate group. The possible variation of the type of bonding of the thiocyanate group as a function of the substituent of the organic base may help to identify parameters characteristic of the ligand which may be correlated with the bonding type Pd–S or Pd–N.

Experimental Section

The following organic ligands were prepared according to the methods described in the literature: 5-methyl-*o*-phenanthroline, 5,6-dimethyl-*o*-phenanthroline, 5-chloro-*o*-phenanthroline,[9] 5-nitro-*o*-phenanthroline,[10] 4,4′-dimethyl-2,2′-bipyridine,[11] and 4-nitropyridine.[12] The other ligands are commercially available.

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(1) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

(2) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(3) J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961).

(4) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(5) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(6) F. Basolo, J. L. Burmeister, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

(7) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).

(8) A. Sabatini and I. Bertini, *ibid.*, **4**, 1665 (1965).

(9) F. Richter and G. F. Smith, *J. Am. Chem. Soc.*, **66**, 396 (1944).

(10) L. P. Hammett, G. H. Walden, Jr., and S. M. Edmonds, *ibid.*, **56**, 1092 (1934).

(11) F. H. Case, *ibid.*, **68**, 2574 (1946).

(12) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

TABLE I
ANALYTICAL DATA FOR THE [PdL_2X_2] COMPLEXES

Complex[a]	Analyses, %					
	Theory			Found		
	N	C	H	N	C	H
[Pd(5-methylphen)($SCN)_2$]	13.43	43.30	2.59	13.40	43.22	2.41
[Pd(5-methylphen)Cl_2]	7.56			7.72		
[Pd(5,6-dimethylphen)($SCN)_2$]	13.00	44.57	2.81	13.05	44.35	2.61
[Pd(5,6-dimethylphen)Cl_2]	7.28			7.36		
[Pd(4,7-dimethylphen)($SCN)_2$]	13.00	44.57	2.81	13.10	44.41	2.58
[Pd(4,7-dimethylphen)Cl_2]	7.28			7.55		
[Pd(5-methyl-6-nitrophen)($SCN)_2$]	15.16	38.99	1.96	15.30	40.12	2.15
[Pd(5-methyl-6-nitrophen)Cl_2]	10.02			10.10		
[Pd(5-chlorophen)($SCN)_2$]	12.81	38.42	1.61	12.65	38.56	1.62
[Pd(5-chlorophen)Cl_2]	7.15			7.16		
[Pd(4,7-diphenylphen)($SCN)_2$]	10.10	56.26	2.90	10.21	56.40	3.02
[Pd(4,7-diphenylphen)($NCS)_2$]	10.10	56.26	2.90	10.23	56.49	3.10
[Pd(4,7-diphenylphen)Cl_2]	5.49			5.61		
[Pd(5-nitrophen)($NCS)_2$]	15.62	37.47	1.57	15.69	37.90	1.63
[Pd(5-nitrophen)Cl_2]	10.43			10.55		
[Pd(4,4′-dimethylbipy)(NCS)(SCN)]	13.78	41.30	2.97	13.79	41.47	2.98
[Pd(4,4′-dimethylbipy)Cl_2]	7.74			7.77		
[Pd(*i*-nicotin)$_2$($SCN)_2$]	11.27	38.65	2.84	11.25	38.43	2.70
[Pd(*i*-nicotin)$_2Cl_2$]	6.19			6.27		
[Pd(4-cyanopy)$_2$($SCN)_2$]	19.50	39.00	1.87	19.62	39.17	1.91
[Pd(4-cyanopy)$_2Cl_2$]	14.52			14.43		
[Pd(4-nitropy)$_2$($SCN)_2$]	17.84	30.60	1.71	17.72	30.48	1.65
[Pd(4-nitropy)$_2Cl_2$]	13.15			13.32		

[a] Abbreviations: phen, *o*-phenanthroline; bipy, 2,2′-bipyridine; *i*-nicotin, methyl ester of isonicotinic acid; py, pyridine. Whenever the symbol NCS^- is written in a compound this designates M–NCS bonding, whereas SCN^- designates M–SCN bonding.

TABLE II
VIBRATION FREQUENCIES (CM^{-1}) OF THIOCYANATE GROUP IN [$PdL_2(SCN)_2$] COMPLEXES

Complex	C–N stretch	C–S stretch	N–C–S bend
[Pd(phen)($SCN)_2$]	2116 s, sp	697 w	460 mw, 418 m
[Pd(5-methylphen)($SCN)_2$]	2115 s, sp, 2110 s, sp	*a*	453 mw, 418 mw
[Pd(5,6-dimethylphen)($SCN)_2$]	2125 s, sp, 2117 s, sp, 2111 s, sp	700 w	420 mw
[Pd(4,7-dimethylphen)($SCN)_2$]	2115 s, sp, 2102 s, sp	*a*	426 w, 419 w
[Pd(5-methyl-6-nitrophen)($SCN)_2$]	2114 s, sp	*a*	455 w, 421 m
[Pd(5-chlorophen)($SCN)_2$]	2116 s, sp, 2105 s, sp	(700 w)	465 w, 415 m
[Pd(4,7-diphenylphen)($SCN)_2$]	2120 sh, 2113 s, sp	*a*	419 mw
[Pd(4,7-diphenylphen)($NCS)_2$]	2110 s, br	*a*	*b*
[Pd(5-nitrophen)($NCS)_2$]	2120 sh, 2090 s, br	*a*	458 w
[Pd(bipy)($NCS)_2$]	2100 s, br	845 m	458 w
[Pd(4,4′-dimethylbipy)(NCS)(SCN)]	2120 s, sp, 2090 s, br	*a*	452 mw, 458 mw
[Pd(py)$_2$($SCN)_2$]	2112 s, sp	*a*	424 w, (436 s?)
[Pd(*i*-nicotin)$_2$($SCN)_2$]	2117 s, sp	*a*	424 vw
[Pd(4-cyanopy)$_2$($SCN)_2$]	2114 s, sp	702 mw, 696 mw	420 mw
[Pd(4-nitropy)$_2$($SCN)_2$]	2115 s, sp	*a*	427 mw

[a] Band masked by the absorption of the organic ligand. [b] Band masked by the absorption of the organic ligand but not in the range of the S-bonded compounds. Abbreviations: s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder.

The thiocyanate complexes were prepared by dissolving 0.5 mmole of $K_2[Pd(SCN)_4]$ in 30 ml of alcohol (98%) and adding the stoichiometric quantity of ligand dissolved in 20 ml of alcohol. The complexes began to precipitate immediately, and after a short period of agitation they were filtered and washed with alcohol and ether. The respective chlorides were prepared analogously, starting from $K_2[PdCl_4]$ in an alcohol–water mixture as described by Burmeister and Basolo.[7] Analyses of the compounds (N, C, H) are reported in Table I.

The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer Model 337 spectrophotometer.

Results

The assignment of the vibration modes of the NCS group of the thiocyanate complexes has been made by comparison with the analogous chloro complexes (see, for example, Figure 1). The values observed for the frequencies of C–N stretching, C–S stretching, and NCS bending, expressed in cm^{-1}, are reported in Table II. Given the high number of bands from these complexes and their relative intensity compared with those of the thiocyanate group, the C–N stretching frequency has been used, in accordance with what has been found previously,[8] for determining the type of bonding. The C–S stretching and the NCS bending, when observed, confirm the conclusions thus obtained.

As expected in the *cis* complexes two C–N stretching frequencies are generally observed; sometimes, probably because of accidental degeneracy, only a single band is observed. Only in [Pd(5,6-dimethylphen)($SCN)_2$] are three C–N stretchings observed which can be explained as solid-state effects (factor group splitting).

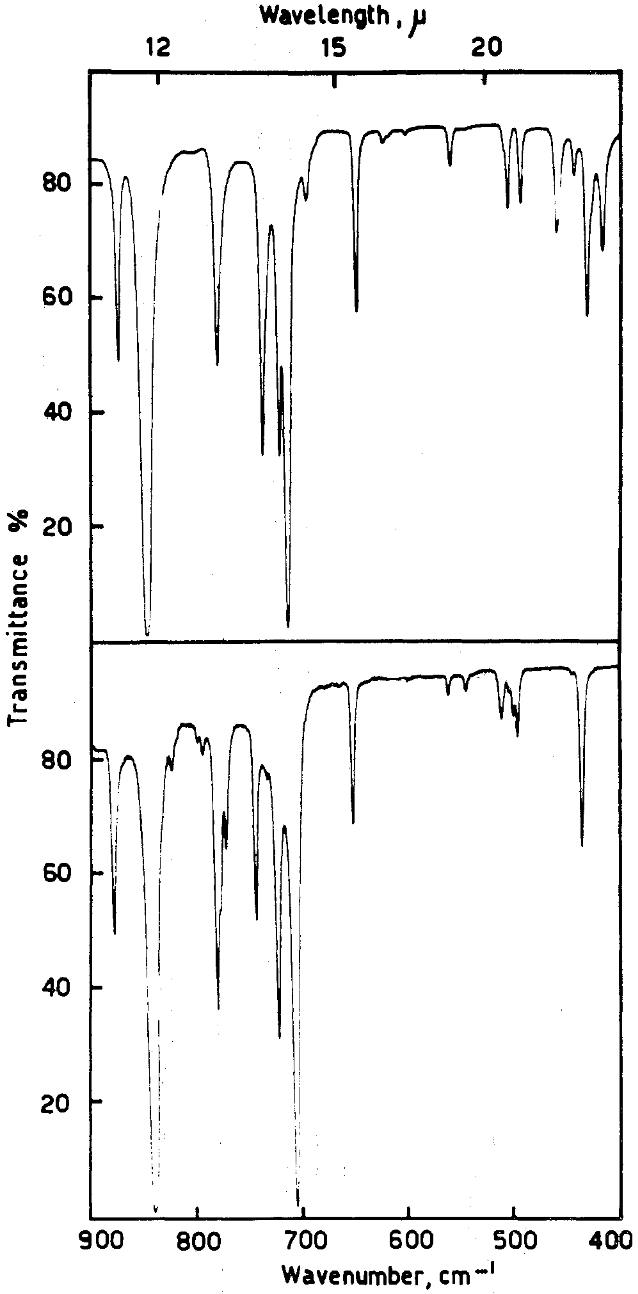

Figure 1.—Spectra of [Pd(phen)(SCN)$_2$] (above) and [Pd(phen)Cl$_2$] (below). The band at 697 in [Pd(phen)(SCN)$_2$] had been assigned as C–S stretching by Burmeister and Basolo.[7]

The values of the frequencies of the absorption bands of a sample of [Pd(4,7-diphenylphen)(SCN)$_2$] prepared at room temperature lead to the conclusion that Pd–S bonding is present. The C–N stretching of a sample of the same compound prepared at 0° has the shape and lies in the range of the C–N stretching of the N-bonded thiocyanate complexes. X-Ray photographs showed that this compound is amorphous. The broadening of the C–N stretching frequency might therefore be attributed to the disorganized structure of the solid compound, but the low value of this band and the absence of the band at 419 cm^{-1}, previously assigned to the NCS bending of the S-bonded isomer, make it seem more probable that we are dealing with an N-bonded thiocyanate complex. This is the first time in the study of the linkage isomers of the thiocyanate group that an N-bonded compound has been isolated at lower temperatures.

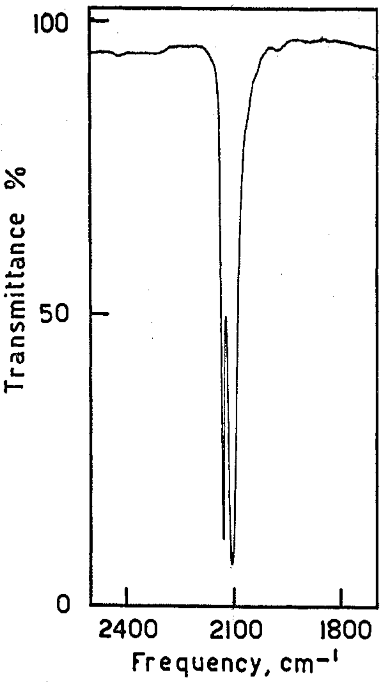

Figure 2.—C–N stretching absorption bands of [Pd(4,4′-dimethylbipy)(SCN)(NCS)].

The spectrum of [Pd(4,4′-dimethylbipy)(NCS)$_2$] shows a sharp band at 2120 cm^{-1} and a broad band at 2090 cm^{-1} (Figure 2). These two bands might be due to a mixture of N- and S-bonded isomers, but the compound prepared at −78° and that recrystallized at +100° from dimethylformamide show the same spectrum. This leads us to believe that we are not dealing with a mixture, but with a single compound. The two C–N stretching bands could then be explained, if we imagine that in the single molecule one NCS group is linked through sulfur and the other through nitrogen. Unfortunately, it has not been possible to study this complex any further because of its poor solubility in common organic solvents. In dimethylformamide, in which it is slightly soluble, dissociation of the complex takes place, as is revealed by the infrared spectrum, which shows the C–N stretching frequency of the free thiocyanate ion. Another possible explanation is that the two absorption bands could correspond to the symmetric and asymmetric C–N stretching frequencies. Although the different shape of the two bands makes more plausible the first interpretation, no definite conclusion can be drawn.

The spectra of the other compounds do not present any complications and indicate clearly the type of bonding.

Discussion

It has been suggested by some authors[4,7] that the bonding M–SCN is stabilized with regard to the bonding M–NCS by π bonding which is formed between the d electrons of the metal and an empty antibonding π orbital located on the sulfur atom of the thiocyanate group. The availability of the metal d electrons for the M–SCN π bond will, however, be reduced by their participation in π back bonding with any strong π-acceptor organic ligands also present in the complex to such an extent that the M–NCS bond may be preferred. Transition from S-bonded to N-bonded thiocyanates may therefore be expected if the π-acceptor capacity of an organic ligand is increased.

It is known that 2,2′-bipyridine and *o*-phenanthroline are capable of forming relatively strong π back bonding with transition metals;[13] accordingly, the [Pd(bipy)(NCS)$_2$] complex exists almost at room temperature as the N-bonded isomer; [Pd(phen)(SCN)$_2$] exists, however, only as the S-bonded compound. By attaching a nitro group to the aromatic ring of this latter ligand, its ability to form π bonds will be increased because of inductive and mesomeric effects (depending on the position in which the nitro group is attached). Accordingly, it is found that the complex with 5-nitro-*o*-phenanthroline gives rise to an N-bonded compound, in spite of the fact that the position of attachment of the nitro group is least favorable for withdrawing π electrons from the aromatic nitrogens. On the other hand the methylphenanthrolines give rise only to S-bonded complexes, in accordance with the fact that the methyl group donates electrons to the aromatic nucleus through an inductive effect or hyperconjugation.

On the basis of the results reported above, it seems that the nucleus of bipyridine tends to draw the d electrons from the palladium atom more strongly than *o*-phenanthroline. This is indirectly confirmed by the values of pK_a:[14] *o*-phenanthroline, 4.96; 4,7-dimethyl-*o*-phenanthroline, 5.94; 5-methyl-*o*-phenanthroline, 5.23; 5-chloro-*o*-phenanthroline, 4.26; 5-nitro-*o*-phenanthroline, 3.57; 2,2′-bipyridine, 4.35; and pyridine, 5.18. The value of pK_a is related to the density of charge on the nitrogen atoms in a series of analogous compounds. The fact that bipyridine has a lower pK_a value than *o*-phenanthroline means that the electronic cloud is more concentrated on the nitrogens of *o*-phenanthroline than on those of 2,2′-bipyridine. This difference in electronegativity could account for the greater tendency to form π bonding on the part of 2,2′-bipyridine in comparison with *o*-phenanthroline. This interpretation of pK_a obviously includes and accounts for the mesomeric and inductive effects, which were discussed previously.

In the case of [Pd(5-Cl-*o*-phen)(SCN)$_2$], although the 5-chloro-*o*-phenanthroline has a pK_a value of the same order of magnitude as 2,2′-dipyridine, only the S-bonded complex has been obtained.

This shows that the scale of the pK_a values alone is not sufficient to explain the bonding type. This is also evident in the case of [Pd(5-CH$_3$-6-nitro-*o*-phen)(SCN)$_2$], where attaching a methyl group to the 6-nitro-*o*-phenanthroline causes again the change of the bond type from Pd–N to Pd–S, although presumably the pK_a value of the ligand does not change too much.

Another important factor which determines the bond type can be the formation energy of the metal–ligand π bond. Even though 4-nitropyridine has a very low pK_a value, it does not succeed in stabilizing Pd–N bonding. This complex probably has the *trans* configuration, and consequently the formation energy of the π bond with the palladium is inferior to that in the *cis*-planar configuration with condensed rings like that of *o*-phenanthroline or 2,2′-bipyridine. On the basis of the same energy considerations, 4,7-diphenyl-*o*-phenanthroline gives rise to an N-bonded compound at low temperatures. The two phenyls in the 4 and 7 positions, which are the most favorable for conjugation with the ring of *o*-phenanthroline, can, at low temperature, partially conjugate with the system and increase the energy of formation of the π back bonding. At higher temperatures thermal motion of the phenyl rings does not favor conjugation and as a consequence Pd–S bonding is stabilized.

The arguments, discussed above, also account for the results previously found:[7,8] the phosphines give N-bonded compounds, the triphenylarsine both N- and S-bonded isomers, the trialkylarsines and the triphenylstibine only S-bonded compounds. Chatt and Wilkins[15] have found that phosphines, arsines, and stibines, combined with platinum, form π bonds of the same energy. We believe that, in accordance with the above, the stronger electronegativity of phosphorus compared with arsenic and antimony, and of arsenic linked with three aryl groups compared with arsenic linked with three alkyl groups, gives an account of the behavior of the thiocyanate group with respect to these ligands, assuming that the formation energies of the bonds do not differ too much.

Acknowledgment.—The authors thank Prof. L. Sacconi for helpful discussions and Dr. J. Gelsomini for the microanalyses. Thanks are expressed to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

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(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 189.

(14) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

(15) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).