

Antisymbiosis and the *trans*-Influence in Gold(I) Thiocyanate Complexes

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*Au–NCS/Au–SCN ratios have been determined, using infrared spectroscopy ($\nu_{C\equiv N}$ integrated absorption intensity ratios) for a series of linear L–Au–(thiocyanate) complexes dissolved in a variety of solvents. The observation that the Au–NCS/Au–SCN ratio increases as the *trans* influence of the L ligand increases is completely in concert with the trend predicted by the antisymbiotic *trans* influence theory. This result is especially meaningful, in view of the fact that steric control of the thiocyanate's bonding mode is non-existent in these complexes. Solvent effects, though non negligible, did not vary in a regular fashion. Only the S-bonded isomer of each complex is present in the solid state. The far infrared solution spectra of the thiocyanate complexes, most of their chloro analogs, and a few of their cyano analogs have been recorded and analyzed for pertinent peak assignments. Reaction of $[Au(P(C_6H_5)_3)_2SCN]$ with an equivalent amount of $P(C_6H_5)_3$ in 1,2-dichloroethane produces significant amounts of both a tricoordinate complex, $[Au(P(C_6H_5)_3)_2(SCN/NCS)]$ and its ionized form, $[Au(P(C_6H_5)_3)_2]SCN$. The former complex exhibits a much larger degree of N-bonding than any of the dicoordinate LAu(thiocyanate) complexes, probably due, at least in part, to some steric crowding.*

Introduction

Linearly dicoordinated Au(I) complexes offer a number of advantages over the complexes of other class (b) metals that have a square planar geometry, such as Pt(II), Pd(II), Ir(I) and Rh(I), in studying the electronic control of the bonding mode of ambidentate ligands such as SCN^- and $SeCN^-$. Since the ligands are at opposite sides of the molecule, there can be no steric control [1–3] of the bonding mode of the thiocyanate and selenocyanate ions. The ligands are also in the proper position to investigate a *trans* influence [2–4] on the bonding mode. Since

most of these Au(I)–thiocyanate complexes are neutral, they would not be susceptible to counter-ion control [2, 3, 5] of the bonding mode. A fourth advantage would be that the infrared spectra of the complexes should be relatively simple to analyze because there are only two ligands present.

The concept of the antisymbiotic *trans* influence [4] predicts that the site *trans* to a strong *trans* director will become harder in complexes of class (b) metals. Unfortunately, much of the work previously reported [2, 3] has involved the use of bulky ligands, such as alkyl and aryl phosphines, in square planar thiocyanate and selenocyanate complexes. Separation of the electronic and steric control variables becomes quite difficult in these cases, and tends to destroy the usefulness of the thiocyanate and selenocyanate ions as probes to determine if a particular coordination site is hard or soft. Indeed, the question of electronic *versus* steric control of the thiocyanate's bonding mode, especially in phosphine-containing complexes of Pd(II) and Pt(II), has been the source of considerable controversy [2, 3] for almost two decades. Happily, the linear Au(I)–thiocyanate complexes utilized in this study [6] are free of these complications, and serve as an ideal testing ground for probing the antisymbiotic *trans* influence theory [4].

Experimental Section

Preparation of Compounds

Trimethylphosphine [7], AuCN [8, 9], $[Au(P(CH_3)_3)_2CN]$ [10], $K[AuCl_4]$ [11] (This complex was converted to the corresponding tetramethylammonium salt by adding excess tetramethylammonium chloride to an aqueous solution of $K[AuCl_4]$. The yellow product, which precipitated immediately, was isolated by filtration, washed with water and dried *in vacuo*. Recrystallization from acetone produced a crystalline product). $K[Au(SCN)_2]$ [12], $[Au(Z(C_6H_5)_3)X]$ [13] ($Z = P$, $X = Cl, SCN, SeCN$; $Z = As$, $X = Cl, SCN$; $K[AuCl_4]$ was used as the starting material instead of $HAuCl_4 \cdot 3H_2O$ in each

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case), and $[\text{Au}(\text{P}(\text{OCH}_3)_3)\text{Cl}]$ [14] were prepared according to methods given in the literature.

Chloro(trimethylphosphine)gold(I); [Au-(P(CH₃)₃)Cl]

A slight excess of $\text{P}(\text{CH}_3)_3$ was added to a solution containing 4.0 g of $[(\text{CH}_3)_4\text{N}][\text{AuCl}_4]$ dissolved in 50 ml of ethanol. After stirring for one hr, the light yellow precipitate was isolated by filtration and washed with water. The damp complex was recrystallized from 2-propanol, giving a white product. The complex was identified by comparison of its infrared spectrum with published results [15]. Yield: 45%. Dec. pt: 228–229 °C.

Cyano(triphenylphosphine)gold(I); [Au-(P(C₆H₅)₃)CN]

Cyanogold(I) (0.200 g) was slurried in 10 ml of CHCl_3 containing 0.235 g of triphenylphosphine and boiled to dryness. As soon as it was dry, the product was dissolved in 10 ml of CHCl_3 . Unreacted AuCN was removed by filtration, and the colorless product was precipitated by the addition of excess petroleum ether. Yield: 86%. Dec. pt: 204–205° (Lit. 203.5–204° [16] and 197–198° [17]). *Anal.* Calcd. for $\text{C}_{19}\text{H}_{15}\text{AuNP}$: C, 47.02; H, 3.12; P, 6.38. Found: C, 46.89; H, 3.27; P, 6.53.

Thiocyanato(trimethylphosphine)gold(I); [Au-(P(CH₃)₃)SCN]

A slight excess of KSCN was added to an acetone solution (15 ml) containing 0.10 g of $[\text{Au}(\text{P}(\text{CH}_3)_3)\text{Cl}]$. The resulting potassium chloride was removed by filtration and the volume of the filtrate was reduced to dryness by boiling under reduced pressure. This was redissolved in 15 ml of chloroform, filtered to remove the excess KSCN, and the colorless product was precipitated by the addition of excess petroleum ether. The light sensitive complex was isolated by filtration, washed with petroleum ether and air dried. *Anal.* Calcd. for $\text{C}_4\text{H}_9\text{AuNPS}$: C, 14.51; H, 2.74; Au, 59.48; N, 4.23. Found: C, 14.57; H, 2.76; Au, 59.19; N, 4.35.

Thiocyanato(triphenylphosphite)gold(I); [Au-(P(OC₆H₅)₃)SCN]

Triphenylphosphite (0.50 g) and $\text{K}[\text{Au}(\text{SCN})_2]$ (0.65 g) were added to 15 ml of methanol. When the solid had dissolved, 25 ml of ethylene glycol was added, and the solution was cooled in an ice bath. The colorless product was precipitated by the slow addition of 50 ml of water. After stirring for 30 min, the complex was isolated by filtration, washed with water and dried *in vacuo*. The product was redissolved in 10 ml of benzene, filtered, cooled in an ice bath and reprecipitated by the slow addition of hexane. After stirring for 30 min, the complex was again isolated by filtration, washed with hexane and

dried *in vacuo*. The complex was stored in a refrigerator. Yield: 77%. m.p. 55–56°. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{15}\text{AuNO}_3\text{PS}$: C, 40.36; H, 2.67; Au, 34.84. Found: C, 40.32; H, 2.77; Au, 34.65.

Thiocyanato(N,N'-ethylenethiourea)gold(I); [Au-(SCNHCH₂CH₂NH)SCN]

$\text{N,N'$ -ethylenethiourea (0.17 g) and $\text{K}[\text{Au}(\text{SCN})_2]$ (0.65 g) were dissolved in 10 ml of methanol, and 20 ml of ethylene glycol was added. After cooling on an ice bath, 50 ml of water was slowly added to precipitate the white product and the mixture was stirred for 30 min. The white product was isolated by filtration washed with water and dried *in vacuo*. The complex was redissolved in 20 ml of acetone, filtered, cooled in an ice bath and reprecipitated by the slow addition of hexane. After stirring for 30 min, the product was isolated by filtration, washed with hexane and dried *in vacuo*. Yield: 97%. m.p. 160–167° (decomposition). *Anal.* Calcd. for $\text{C}_4\text{H}_6\text{AuN}_3\text{S}_2$: C, 13.45; H, 1.69; Au, 55.14. Found: C, 13.71; H, 1.82; Au, 55.37.

Thiocyanato(dibenzylsulfide)gold(I); [Au-(S-(CH₂C₆H₅)₂)SCN]

Dibenzylsulfide (0.30 g) and 0.50 g of $\text{K}[\text{Au}(\text{SCN})_2]$ were dissolved in 5 ml of ethanol. To this was added 20 ml of ethylene glycol, followed by the slow addition of 75 ml of water. When the white complex has coagulated, it was isolated by filtration, washed with water and dried under a high vacuum. The product was dissolved in 15 ml of dichloromethane, AuSCN was removed by filtration, and the product washed with petroleum ether and air dried. Since the complex dissociates somewhat, forming insoluble AuSCN ($\nu_{\text{C}\equiv\text{N}}$ infrared band at 2160 cm^{-1}), it was not analyzed. A small amount of $\text{S}(\text{CH}_2\text{C}_6\text{H}_5)_2$ was added to the solutions of this complex used in this study. Yield: 69%.

Physical Measurements

Solid state infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 337 spectrophotometer using KBr plates. A Perkin-Elmer 180 spectrophotometer was used to measure high resolution solid state Nujol mull and solution infrared spectra in the $\nu_{\text{C}\equiv\text{N}}$ region and in the far infrared to 180 cm^{-1} . When the solvent used was either dichloromethane or benzene, matched 1.00 mm NaCl solution cells were used. For all other solvents, matched 0.5 mm polyethylene cells were used. These are transparent in the regions, 2170–2040 cm^{-1} and 570–180 cm^{-1} , in which they were employed. They were used to remove the possibility of chloride, from the NaCl windows, substituting for thiocyanate [18, 19]. The cells were constructed from 0.027 inch thick sheets of polyethylene, purchased from Barnes Engineering Co., Stamford, Connecticut, cut to fit

Perkin-Elmer sealed liquid absorption cell mounts. The windows were separated with 0.5 mm lead spacers. Since the cell was so thin, three 1/16 inch thick aluminum spacers were made and placed below the cell to allow it to be held in the mount. A set was matched by the addition of 0.015 and 0.025 mm spacers to the thinnest cell until the base line was as flat as possible in the $\nu_{\text{C}\equiv\text{N}}$ stretching region when DMF was used as the solvent. The cells leaked badly in the IR beam with solvents having low boiling points. Since spectra of the far infrared region took longer to record than those of the $\nu_{\text{C}\equiv\text{N}}$ stretching region, dibromomethane (b.p. 97 °C) was the solvent used for solution spectra recorded in this region. CsI plates were used when Nujol mull spectra were recorded in the far infrared region. All of the aprotic solvents used, except for DMF and DMSO, were distilled, nitrobenzene being distilled over P_4O_{10} , prior to use. All solvents except dichloromethane were stored over Linde 4A molecular sieves.

The ratios of the $\nu_{\text{C}\equiv\text{N}}$ integrated absorption intensities of N-bonded/S-bonded thiocyanates were calculated as follows. The infrared $\nu_{\text{C}\equiv\text{N}}$ stretching region was recorded on a Perkin-Elmer Model 180 spectrophotometer under high resolution, using the linear absorbance mode rather than the linear transmittance mode. The low energy tail of the high energy absorption band was drawn in (an estimate) and the resulting envelopes were traced on paper. These were carefully cut out and weighed on a Mettler balance. The weight of the N-bonded band was divided by that of the S-bonded band, giving an N-bonded/S-bonded ratio.

The melting and decomposition points were measured on a Fisher-Johns Melting Point Apparatus and are uncorrected. Elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, Germany. Gold was analyzed as a residue.

Results and Discussion

When recording the dichloromethane solution infrared spectrum of $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$ in the $\nu_{\text{C}\equiv\text{N}}$ stretching region, two absorption bands were observed, instead of the one previously reported by DeStefano and Burmeister [13]. It was unfortunate that they used 0.1 mm solution cells instead of the 0.5 mm and 1.0 mm solution cells used in this study. The solutions used were also less concentrated. At the time, there was no idea that two $\nu_{\text{C}\equiv\text{N}}$ absorption bands could be present, since the solid state infrared spectrum exhibited only one S-bonded $\nu_{\text{C}\equiv\text{N}}$ band and hence, the second, broader, less intense band observed in the present solution infrared spectrum was missed. With such a simple complex, we immediately realized that the second, lower energy

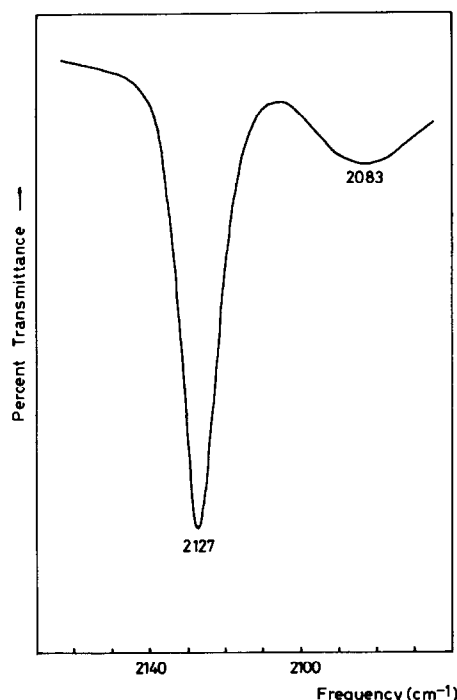


Fig. 1. $\nu_{\text{C}\equiv\text{N}}$ bands exhibited by $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$ (10^{-2} M dichloromethane solution).

band had to be the $\nu_{\text{C}\equiv\text{N}}$ absorption band of the nitrogen bonded isomer. The higher energy band had previously been identified by DeStefano and Burmeister [13] to be that of an S-bonded thiocyanate by the measurement of its integrated absorption intensity ($1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ in dichloromethane), which is lower than that of the free ion value [2]. Figure 1 shows the infrared spectrum recorded in this region for a 10^{-2} M dichloromethane solution of $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$, using the larger cells.

The $\nu_{\text{C}\equiv\text{N}}$ bands exhibited by $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$ underwent small shifts when recorded in other solvents (e.g., benzene, 2131 and 2076 cm^{-1} ; acetone, 2130 and 2084 cm^{-1} ; acetonitrile, 2128 and 2088 cm^{-1}). The relative intensities of the two bands were also sensitive, to a small degree, to the nature of the solvent in which the complex was dissolved. However, no trend that inversely or directly followed the dielectric constant of the solvent was apparent. Therefore, there is no solvent effect of the type described by Burmeister *et al.* [20] or Marzilli [21]. In this context [2, 3], if there were a solvent effect, the increase in intensity of the band ascribed to the N-bonded isomer would follow the dielectric constant change, either directly [21] or inversely [20].

With the discovery of the equilibrium involving the linkage isomers of $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$, it seemed

TABLE I. Au–NCS/Au–SCN Ratios for a Series of [LAu(thiocyanate)] Complexes in Solution.

Complex	Au–NCS/Au–SCN Ratio ^a	Other Solvents Used
[Au(P(OC ₆ H ₅) ₃)SCN]	1.57	b,c,d
[Au(P(CH ₃) ₃)SCN]	0.67	c,d,e,f,g
[Au(P(C ₆ H ₅) ₃)SCN]	0.52	b,c,d,e,f,g
[Au(As(C ₆ H ₅) ₃)SCN]	0	b,c,d,e,f,g
[Au(S(CH ₂ C ₆ H ₅) ₂)SCN]	0	c
[Au(etu)SCN] ^h	0	f
[Au(P(C ₆ H ₅) ₃)SeCN]	0	b,c,d,e,f,g

^aRatio measured in ClCH₂CH₂Cl (see text).^bBenzene.^cNitrobenzene.^dAcetonitrile.^eDichloromethane.^fAcetone.^gDMSO. ^hetu = ethylenethiourea.

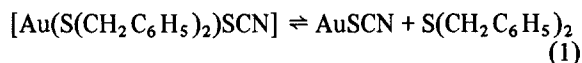
pertinent to record the spectra of similar complexes in a variety of solvents. Since the equilibrium was reached before the infrared spectrum could be recorded, it was necessary to find a physical method to measure the degree of isomerization. The ratio of the integrated absorption intensities of the two $\nu_{\text{C}\equiv\text{N}}$ infrared absorption bands was chosen. Table I lists the complexes investigated (in the order of decreasing *trans* influence of the L ligand), and the ratios measured for the 1,2-dichloroethane solutions. Also listed are the other solvents used.

It should be noted that the N-bonded isomer is a minor or non-existent component in all of the solutions, since the integrated absorption intensity of the $\nu_{\text{C}\equiv\text{N}}$ band of an N-bonded thiocyanate is generally about an order of magnitude larger [2] than that of an S-bonded thiocyanate. Nonetheless, it is clear that the proportion of the N-bonded isomer present in a given solvent increases as the *trans*-influence of the L ligand increases, completely in accord with Pearson's antisymbiotic *trans*-influence principle [4]. The stronger the *trans* director, the harder the remaining site becomes and, consequently, the greater the Au–NCS/Au–SCN ratio.

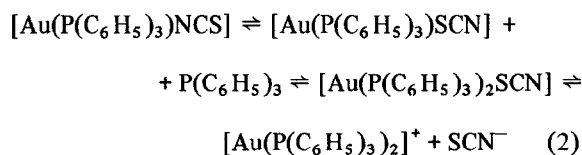
If the assumption is made that the intensity of the N-bonded isomer is exactly 10 times that of the S-bonded isomer, then the percent of the N-bonded isomer present at equilibrium can be calculated as follows: $10X/(1 - X) = \text{Au–NCS/Au–SCN ratio}$; $100X = \text{percent of the N-bonded isomer present in solution}$. Calculated in this manner, the percent of the N-bonded isomer present at equilibrium in 1,2-dichloroethane for three of the complexes is listed below.

Complex	Percent N-bonded
[Au(P(OC ₆ H ₅) ₃)SCN]	13.4
[Au(P(CH ₃) ₃)SCN]	6.3
[Au(P(C ₆ H ₅) ₃)SCN]	4.9

As mentioned in the Experimental Section, it was necessary to add a small amount of dibenzylsulfide to a solution of [Au(S(CH₂C₆H₅)₂)SCN] in order to dissolve it completely, since the equilibrium,



appears to occur in solution. To see if this addition of dibenzylsulfide altered the results, equivalent amounts of [Au(P(C₆H₅)₃)SCN] and P(C₆H₅)₃ were dissolved in 1,2-dichloroethane and the infrared spectrum of the resulting solution in the $\nu_{\text{C}\equiv\text{N}}$ stretching region was recorded (Fig. 2). The solution spectrum of [Au(P(C₆H₅)₃)SCN] alone in this solvent shows $\nu_{\text{C}\equiv\text{N}}$ absorption bands at 2128 and 2082 cm⁻¹. The shift of the band at 2082 to 2091 cm⁻¹ and the appearance of the band at 2057 cm⁻¹, which is attributable [2] to ionic thiocyanate, indicates that new species are present in the solution. The reaction can be written as follows:



The intensity of the N-bonded absorption bands (2091 cm⁻¹) is much stronger than that observed for the solution of pure [Au(P(C₆H₅)₃)SCN]. The two triphenylphosphines appear to make the third coordination site relatively harder. Since all three ligands would be bonded to the gold *via* sp² hybrid orbitals on the gold, it is possible that two phosphines could exert a stronger influence on the remaining site than just one phosphine, possibly due, at least in part, to steric crowding. The analogous complex, [Au(P(C₆H₅)₃)₂Cl], has been prepared [22], providing

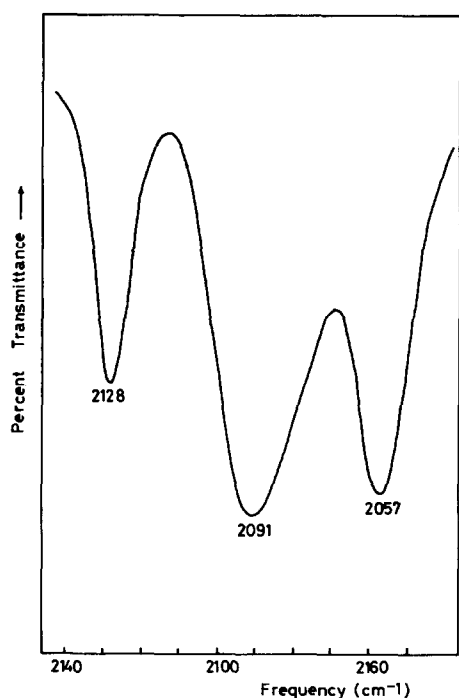


Fig. 2. $\nu_{C\equiv N}$ bands exhibited by 1:1 mixture of $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$ and $\text{P}(\text{C}_6\text{H}_5)_3$ ($10^{-2} M$ 1,2-dichloroethane solution).

further support for the existence of the proposed three coordinate complex.

The solid state spectra of the $[\text{AuLSCN}]$ complexes show that only the S-bonded isomer is present in the solid. Apparently the crystal packing favors the geometry of this isomer.

It should be noted that $[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SeCN}]$ is totally Se-bonded in solution. Selenium is softer than sulfur and, hence, a stronger *trans*-director. As such, it can better compete with the phosphine for the bonding orbitals on the gold, making the gold-phosphorus bond weaker than when the gold is

TABLE II. Solution Far Infrared Spectra (cm^{-1}) of AuLCl and AuLCN Complexes in CH_2Br_2 ($10^{-1} M$).

Complex	$\nu_{\text{Au-Cl}}$	$\nu_{\text{Au-P}}$	
$[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3\text{Cl})]$	328	^a	
$[\text{Au}(\text{As}(\text{C}_6\text{H}_5)_3\text{Cl})]$	329	—	
$[\text{Au}(\text{P}(\text{OCH}_3)_3\text{Cl})]$	335	^a	
$[\text{Au}(\text{P}(\text{CH}_3)_3\text{Cl})]$	325	381	
Complex	$\nu_{\text{Au-CN}}$	δ_{AuCN}	$\nu_{\text{Au-P}}$
$[\text{Au}(\text{P}(\text{CH}_3)_3\text{CN})]$	414	348	363
$[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3\text{CN})]$	408	^a	^a

^a Unknown or unobserved.

TABLE III. Solution Far Infrared Spectra (cm^{-1}) of AuLXCN Complexes in CH_2Br_2 ($10^{-1} M$) ($X = \text{S}, \text{Se}$).

Complex	$\nu_{\text{Au-XCN}}$	δ_{SCN}	$\nu_{\text{Au-P}}$
$[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SCN}]$	299	422	^a
$[\text{Au}(\text{As}(\text{C}_6\text{H}_5)_3)\text{SCN}]$	302	420	^a
$[\text{Au}(\text{P}(\text{CH}_3)_3)\text{SCN}]$	296	454, 422	371
$[\text{Au}(\text{P}(\text{OC}_6\text{H}_5)_3)\text{SCN}]$	303	453, 418	390
$[\text{Au}(\text{S}(\text{CH}_2\text{C}_6\text{H}_5)_2)\text{SCN}]$	304	^a	^a
$[\text{Au}(\text{SC}(\text{NHCH}_2)_2)\text{SCN}]$	304	^a	^a
$[\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\text{SeCN}]$	218	372	^a

^a Not observed.

bonded to the sulfur atom in thiocyanate. With the weakened gold-phosphorus bond, the phosphorus becomes a weaker *trans*-director.

The far infrared spectra of a number of the neutral gold(I) complexes were recorded. The results are shown in Tables II and III. The assignments are based on a comparison of the spectra of the chloro, cyano and thiocyanato complexes.

Williamson and Baird [14] have made an extensive study of gold(I)-halide stretching frequencies, varying the neutral ligand in AuLX complexes. They have used these frequencies to arrive at a list of L showing a decreasing *trans*-influence. In most cases, solid state spectral data were cited. They also used many values from the literature. The four chloro complexes whose solution far infrared spectra were measured in this study did not follow their order, as shown below.

$\nu_{\text{Au-Cl}}$ for AuLCl Complexes (cm^{-1})

L	W. and B. [14]	This Work
$\text{As}(\text{C}_6\text{H}_5)_3$	338	329
$\text{P}(\text{C}_6\text{H}_5)_3$	333	328
$\text{P}(\text{OCH}_3)_3$	326	335
$\text{P}(\text{CH}_3)_3$	311	325

The differences among the several gold-chloride stretches become much smaller in solution than they are in the solid state. The frequencies recorded for the solid state samples are probably altered by crystal lattice effects. The gold-thiocyanate stretches also do not show much of a variation. The ligand that does show a significant change is trimethylphosphine:

$\nu_{\text{Au-P}}$ for $\text{Au}(\text{P}(\text{CH}_3)_3)\text{X}$ Complexes

X	$\nu_{\text{Au-P}}$ (cm^{-1})
—Cl	381
—SCN	371
—CN	363

TABLE IV. Infrared Spectrum^a (cm⁻¹) of K[Au(SCN)₂].

Assignment	Wavenumber
$\nu_{\text{AuSC}\equiv\text{N}}$	2120 s
	2115 s
	2106 s
$2\delta_{\text{SCN}}$	887 w
	874 w
$\nu_{\text{AuS}-\text{CN}}$	722 w
	711 w
	707 w
	705 w
δ_{SCN}	459 w
	438 w
$\nu_{\text{Au}-\text{SCN}}$	303 w

^aNujol mull.

The stronger *trans*-directing X becomes, the lower in energy $\nu_{\text{Au}-\text{P}}$ becomes and, hence, the weaker the gold-phosphorus bond becomes. This helps to explain why [Au(P(C₆H₅)₃)SeCN] is only selenium bonded.

The complex K[Au(SCN)₂] has not previously been analyzed *via* infrared spectroscopy. While the sample was not analyzed elementally, and its spectrum showed extensive solid state splitting, the results shown in Table IV clearly show that the thiocyanates are sulfur bonded, as certainly would be expected in a gold(I) complex. The frequency of the $\nu_{\text{C}-\text{S}}$ stretch identifies [2] the bonding mode of the thiocyanate. Since it is lower than that found in the free ion, the ligands are sulfur bonded.

The results of this study follow the results exhibited by other class (b) metal systems [2, 3] and add further support to the concept of the antisymbiotic *trans* influence [4] as being the primary electronic effect which causes certain coordination sites on class (b) metals to exhibit class (a) behavior. When a soft ligand is placed *trans* to the thiocyanate, as in AuLSCN, the stronger the *trans* director L becomes, the more N-bonding is observed, which is exactly what would be expected. In this case, steric control of the bonding mode of the thiocyanate does not interfere with the interpretation of the results.

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