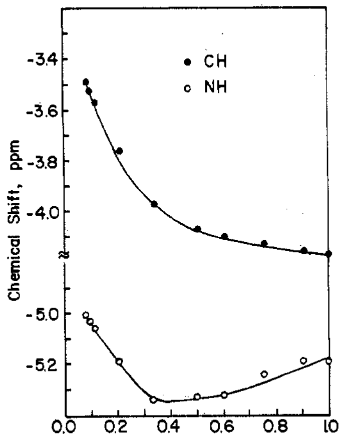

Figure 3. Proton chemical shifts of *cis*-Co(gly)$_3$ at 100 MHz and 30°. Tetramethylammonium chloride was used as the internal standard, and the chemical shift was measured at a scale on which the methyl group of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was taken as zero.

values for the three different NH_2 groups in *trans*-Co(gly)$_3$ are 39.4 ± 0.5, 37.8 ± 0.5, and 42.5 ± 0.2 ppm, respectively, from $^{15}NH_4^+$ in the same solution. It was determined from the double-resonance experiment that the three nitrogens correspond to the three $-NH_2$ groups that have proton chemical shifts at −6.66, −5.28, and −5.28 ppm, respectively (in contrast, the three ^{14}N peaks in *trans*-Co(gly)$_3$ were found to be unresolvable and appeared at 36 ± 7 ppm from $^{14}NH_4^+$ [18]). The ^{15}N-^1H coupling constants are all 72 ± 2 Hz for the NH_2 group and not resolvable for N-C-H. Again the ^{15}N chemical shifts did not change with the acid concentration from $D_2O:D_2SO_4 = 0$ to 8, indicating that the shielding of the nitrogen nucleus is not affected by the change in the second coordination sphere, in contrast to proton and the cobalt nucleus. This indicates that there is no appreciable change in the two factors that determine the nitrogen chemical shift in cobalt(III) complexes,[18] namely, the mixing of excited states and the difference in charge distribution (or the changes are in opposite directions and exactly cancel each other, which is unlikely). Those two kinds of changes are larger at the cobalt and the hydrogen nuclei, respectively, so that appreciable variations in their chemical shifts were observed.

Registry No. *cis*-Co(gly)$_3$, 21520-57-0; *trans*-Co(gly)$_3$, 19963-68-9; ^{15}N-enriched *trans*-Co(gly)$_3$, 38656-89-2; Co(en)$_3$Cl$_3$, 13408-73-6; [Co($^{15}NH_3$)Cl](ClO$_4$)$_2$, 38656-88-1; cobalt, 7440-48-4; ^{15}N, 14390-96-6.

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Complexes of Silver(I) Thiocyanate with Some Tertiary Phosphines, Triphenylarsine, and Triphenylstibine[1]

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In the growing literature on thiocyanate complexes of transition metal ions and the ambidentate nature of the thiocyanate ion, very little has appeared to date on complexes with silver(I) ion. Turco and coworkers[2-5] have prepared silver thiocyanate complexes with a few trialkylphosphines and Capacchi and coworkers[6] have reported a silver thiocyanate complex with thiosemicarbazide. This paper reports on the synthesis and some properties of a number of new silver(I) thiocyanate complexes.

Experimental Section

Analyses. The carbon and hydrogen microanalyses were performed by Crobaugh Laboratories. Silver analyses were performed in our laboratory by an electrogravimetric procedure. This procedure entailed the digestion of the sample by the method described by Norwitz.[7] The digestion was followed by electrodeposition of the metal on a platinum gauze electrode from a basic cyanide solution. The melting points were determined with a Fisher-Johns melting point apparatus. Molecular weight determinations were carried out with a Model 301A Mechrolab Inc. vapor pressure osmometer at 37°. The latter was calibrated with solutions of benzil in acetone and chloroform.

Infrared Spectra. The infrared spectra were measured over the 4000-400-cm^{-1} region on a Perkin-Elmer Model 621 spectrophotometer. All samples were prepared as Nujol or Halocarbon mulls and recorded using potassium bromide windows. The accuracy and reproducibility of the reported band maxima, which were taken from the frequency counter, were estimated to be well within ±2 cm^{-1}.

Reagents. Most of the reagents used in this investigation were commercially available and used as such without further purification. The few exceptions included the benzil, acetone, and chloroform used in the molecular weight studies. Benzil was purified by vacuum sublimation at 90° (oil bath temperature). Reagent grade acetone was dried 48 hr over anhydrous calcium sulfate and distilled at 48° while the chloroform was dried over calcium hydride for 24 hr and distilled at 54°.

Diethylphenylphosphine, PEt_2Ph. The preparation of this ligand was carried out under a nitrogen atmosphere in diethyl ether by the method of Adams and Raynor.[8] The product was distilled at 75-85° and 6 mm (reported value: 96-97° (10 mm)[9]).

Diphenylethylphosphine, PPh_2Et. This ligand was likewise prepared by the method of Adams and Raynor.[8] The crude product was purified by distillation at 105-107° (0.2 mm) (reported value: 129-132° (0.7 mm)[10]).

Preparation of Complexes. With the exceptions of the trimethylphosphine, tri-*n*-butylphosphine, diethylphenylphosphine, and diphenylethylphosphine adducts, in which the preparations were carried out under a nitrogen atmosphere, no special techniques or procedures were employed. The analytical data for the complexes have been included in Table I.

Thiocyanatotrimethylphosphinesilver(I), $AgCNS\cdot PMe_3$. About 3 ml (~31.5 mmol) of PMe_3 was vapor transferred into a frozen, degassed aqueous solution containing 4.47 g (26.3 mmol) of $AgNO_3$ and excess KSCN. After warming to room temperature, followed by 5 min of vigorous shaking, the white product obtained was separated by filtration, washed with 0.25 *M* KSCN and then with water, and finally dried in a desiccator over anhydrous $CaSO_4$. The compound was recrystallized from acetone, in which it was only very slightly soluble, to yield colorless, needlelike crystals.

Thiocyanatotri-*n*-butylphosphinesilver(I), $AgCNS\cdot P(n\text{-}Bu)_3$. Ten milliliters (38.5 mmol) of $P(n\text{-}Bu)_3$ was added to 20.0 g (118.0 mmol) of $AgNO_3$ dissolved in 300 ml of a nitrogen-purged water-ethanol (3:1) solution containing excess KSCN. This mixture was vigorously stirred for 2 hr after which time the white product was separated by filtration and washed with 0.25 *M* KSCN, then with water, and finally

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Table I. Analytical Data for Complexes

Compd	Mp,[a] °C	% calcd			% found			% yield[b]
		Ag	C	H	Ag	C	H	
$\mathrm{AgCNS\cdot PMe_3}$	156–157 dec		19.8	3.76		21.0	4.22	
$\mathrm{AgCNS\cdot P(\mathit{n}\text{-}Bu)_3}$[c]	71	29.3	42.4	7.39	28.9	42.9	7.36	86
$\mathrm{AgCNS\cdot PEt_2Ph}$	109–110		39.9	4.55		39.6	4.52	
$\mathrm{AgCNS\cdot 3PPh_2Et}$	95–96	13.4	63.8	5.61	13.0	63.9	5.64	95
$\mathrm{AgCNS\cdot 2PPh_3}$[d]	197–198	15.6	64.3	4.38	15.5	63.9	5.16	46
$\mathrm{AgCNS\cdot 2AsPh_3}$	188–189 dec	13.9	57.0	3.88	13.6	56.8	4.47	79
$\mathrm{AgCNS\cdot 2SbPh_3}$	162–168 dec		50.9	3.47		49.7	3.60	56

[a] Uncorrected melting point data. [b] Based on silver. [c] The molecular weight measured in acetone was 398 compared to the formula weight of 368. [d] The molecular weight measured in chloroform was 667 compared to the formula weight of 691.

with ice-cold ethanol-acetone (3:1). The compound was recrystallized from aqueous acetone to yield 12.2 g of product. The compound was insoluble in water and absolute ethanol, only sparingly soluble in chloroform, acetonitrile, cyclohexane, tetrahydrofuran, and anhydrous ether, and soluble in acetone. It decomposed in benzene and carbon tetrachloride.

Thiocyanatodiethylphenylphosphinesilver(I), $\mathbf{AgCNS\cdot PEt_2Ph}$, and Thiocyanatobis(diethylphenylphosphine)silver(I), $\mathbf{AgCNS\cdot 2PEt_2Ph}$. To 10.0 g (58.8 mmol) of $\mathrm{AgNO_3}$ dissolved with excess KSCN in 200 ml of nitrogen-purged aqueous acetone (10:1) was added with stirring about 8 ml (62 mmol) of $\mathrm{PEt_2Ph}$. After several minutes, a white product began to form which was separated after an additional 15 min by filtration and washed with 0.25 *M* KSCN, then with water, and finally with a small amount of ice-cold acetone to yield 12.3 g of product. The product was recrystallized from an aqueous acetone solution to give an inseparable mixture of colorless, needlelike crystals and cubiclike crystals. Further experimental evidence for a mixed product was obtained from its infrared spectrum (to be discussed later) and silver analyses which gave values (27.7, 26.1, and 28.2% Ag) between those calculated for $\mathrm{AgCNS\cdot PEt_2Ph}$ (mol wt 332.1; requires 32.5% Ag) and $\mathrm{AgCNS\cdot 2PEt_2Ph}$ (mol wt 498.3; requires 21.6%). When the mixed crystalline product was added to acetone, it rapidly dissolved but shortly thereafter (~1 min) the solution became cloudy. After 0.5 hr, the solution was filtered through a medium-porosity fritted-glass filtering funnel. The filtrate was then set aside for several days, after which time clear cubiclike crystals were collected by filtration and the analysis of this product corresponded to $\mathrm{AgCNS\cdot PEt_2Ph}$.

Thiocyanatotris(diphenylethylphosphine)silver(I), $\mathbf{AgCNS\cdot 3PPh_2Et}$. The reaction, carried out by the preceding method, between 5.00 g (29.4 mmol) of $\mathrm{AgNO_3}$ and 6.50 g (30.4 mmol) of $\mathrm{PPh_2Et}$ produced 7–8 g of product which was recrystallized from an aqueous acetone solution. The compound was soluble in acetone, benzene, and chloroform and insoluble in ethanol, carbon tetrachloride, diethyl ether and cyclohexane.

Thiocyanatobis(triphenylphosphine)silver(I), $\mathbf{AgCNS\cdot 2PPh_3}$. Potassium thiocyanate was added to 5.00 g (29.4 mmol) of $\mathrm{AgNO_3}$ in 150 ml of $\mathrm{H_2O}$ with stirring until the AgSCN had completely dissolved. To this solution was added 15.0 g (57.3 mmol) of $\mathrm{PPh_3}$ and the mixture was heated just below the boiling point with vigorous stirring for 24 hr. The white product was separated by filtration, washed with 0.25 *M* KSCN and then with water, and finally dried in a vacuum desiccator. The compound was recrystallized from chloroform to give 9.3 g of product.

Thiocyanatobis(triphenylarsine)silver(I), $\mathbf{AgCNS\cdot 2AsPh_3}$. Employing the procedure used to prepare $\mathrm{AgCNS\cdot 2PPh_3}$, 5.20 g (17.0 mmol) of $\mathrm{AsPh_3}$ was allowed to react with 2.50 g (14.7 mmol) of $\mathrm{AgNO_3}$ to yield 5.22 g of product. The complex was insoluble in a variety of solvents including benzene, absolute ethanol, tetrahydrofuran, heptane, cyclohexane, acetone, acetonitrile, *o*-xylene, carbon tetrachloride, diphenyl ether and chloroform.

Thiocyanatobis(triphenylstibine)silver(I), $\mathbf{AgCNS\cdot 2SbPh_3}$. When 16.5 g (46.7 mmol) of $\mathrm{SbPh_3}$ was allowed to react by the above procedure with 3.70 g (21.8 mmol) of $\mathrm{AgNO_3}$, 10.7 g of white flocculent product was produced. No suitable solvent for recrystallization was found.

Results and Discussion

The silver complexes were light insensitive and stable toward hydrolysis and air oxidation. They could be stored in the presence of air for several months without any noticeable change.

The trialkylphosphine adducts of silver(I) thiocyanate, $\mathrm{AgCNS\cdot PMe_3}$ and $\mathrm{AgCNS\cdot P(\mathit{n}\text{-}Bu)_3}$ were found to have the indicated stoichiometry even when their preparations were carried out with a $\mathrm{PR_3{:}AgSCN}$ molar ratio in excess of 2:1. Likewise, the complexes $\mathrm{AgCNS\cdot 2XPh_3}$ (X = P, As, Sb) gave the indicated stoichiometries regardless of the $\mathrm{XPh_3{:}AgSCN}$ molar ratio used in their syntheses. Attempts to prepare complexes of silver(I) thiocyanate with triphenylamine by methods described in the Experimental Section were unsuccessful, probably due to both steric and basicity effects exerted by the $\mathrm{NPh_3}$ ligand.

The investigation of the complexes of silver(I) thiocyanate with the mixed tertiary phosphines, $\mathrm{PEt_2Ph}$ and $\mathrm{PPh_2Et}$, was undertaken with the expectation that there would be a transitional ligand with which both the 1:1 and 1:2 adducts could be isolated since the trialkylphosphine adducts had 1:1 stoichiometries and the triphenylphosphine adduct was found to have a 1:2 stoichiometry. This was realized for the silver(I) thiocyanate adducts of $\mathrm{PEt_2Ph}$ which gave both $\mathrm{AgCNS\cdot PEt_2Ph}$ and $\mathrm{AgCNS\cdot 2PEt_2Ph}$, although the latter compound was not obtained in a pure form. Diphenylethylphosphine gave $\mathrm{AgCNS\cdot 3PPh_2Et}$. This compound was unexpected in view of the stoichiometry of other adducts with tertiary phosphines.

An explanation of the variance in stoichiometry in passing from $\mathrm{PEt_3}$ to $\mathrm{PPh_3}$ ($\mathrm{AgCNS\cdot PEt_3}$,[3] $\mathrm{AgCNS\cdot PEt_2Ph}$, $\mathrm{AgCNS\cdot 2PEt_2Ph}$, $\mathrm{AgCNS\cdot 3PPh_2Et}$ and $\mathrm{AgCNS\cdot 2PPh_3}$) that is entirely consistent with the experimental data has not been established. The stoichiometries apparently cannot be entirely attributed to steric effects since the more bulky tertiary phosphine ligands show an opposite trend; *e.g.*, $\mathrm{PEt_3}$ gave $\mathrm{AgCNS\cdot PEt_3}$ while $\mathrm{PPh_2Et}$ gave $\mathrm{AgCNS\cdot 3PPh_2Et}$. On the other hand, with the exception of $\mathrm{AgCNS\cdot 3PPh_2Et}$, the relative σ-donor ($\mathrm{PPh_3} < \mathrm{PEt_3} < \mathrm{P(\mathit{n}\text{-}Pr)_3} < \mathrm{P(\mathit{n}\text{-}Bu)_3}$, π-acceptor ($\mathrm{PR_3} < \mathrm{PR_2Ph} < \mathrm{PRPh_2} < \mathrm{PPh_3}$) abilities of the tertiary phosphines given by Grim, *et al.*,[11] would be in accord with the given series since π bonding could relieve excessive negative charge on the metal allowing yet another group to coordinate. It is probable that there are several factors, only two of which have been alluded to here, that influence silver's coordination ability in these complexes.

The majority of the complexes examined in this investigation were not sufficiently soluble to permit molecular weight determinations. The molecular weight of $\mathrm{AgCNS\cdot P(\mathit{n}\text{-}Bu)_3}$ in acetone corresponded to a monomer and that of $\mathrm{AgCNS\cdot 2PPh_3}$ in chloroform also corresponded to a monomer. The former result is in contrast to those obtained by Turco, *et al.*,[3] who found $\mathrm{AgCNS\cdot P(\mathit{n}\text{-}Pr)_3}$ and $\mathrm{AgCNS\cdot P(\mathit{i}\text{-}Pr)_3}$ to have degrees of association of 2.2–3.0 and 2.0 in benzene, respectively. The marked difference between the degree of association of these latter two compounds and $\mathrm{AgCNS\cdot P(\mathit{n}\text{-}Bu)_3}$ is likely to be due to the difference in the solvent properties of benzene ($\epsilon_{25°}$ 2.27) and acetone ($\epsilon_{25°}$ 20.7). As previously

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mentioned it was noted in this work that $AgCNS \cdot P(n\text{-}Bu)_3$ decomposed in the presence of benzene.

As is well known the thiocyanate ion in metal ion complexes can coordinate through the sulfur atom or through the nitrogen atom or can act as a bridging group using both atoms. Infrared criteria for establishing the bonding mode based on frequency ranges observed for three vibrational modes of the thiocyanate ion have been published by Burmeister[12] and others. The Burmeister ranges are given as footnotes to Table II.

If the CN stretch criterion alone were applied to the infrared data obtained for the new silver thiocyanate complexes reported in this paper (Table II), it would be concluded that $AgCNS \cdot PEt_2Ph$, $AgCNS \cdot P(n\text{-}Bu)_3$, and possibly $AgCNS \cdot PMe_3$ were S bonded and that the remaining complexes were N bonded. However, application of the CS stretch criterion where data could be obtained would indicate bridge bonding for all the 1:1 and 1:2 complexes. Support for the presence of bridge bonding in the 1:1 complexes is provided in a report of an X-ray crystallographic study by Panattoni and Frasson[5] of the related compound $AgCNS \cdot P(n\text{-}Pr)_3$. This trialkylphosphine complex contains zigzag polymeric -Ag-SCN-Ag-SCN- chains cross-linked in pairs by Ag-S bonds to form double chains having a stair-step configuration. The reported silver-nitrogen bond distance of 2.10 ± 0.10 Å corresponds to the calculated covalent value but the silver-sulfur bond lengths of 2.83 ± 0.02 and 2.88 ± 0.02 Å are substantially longer than the calculated single-bond covalent value of 2.56 Å. The above was considered to be consistent with a CN stretching frequency of 2090 cm^{-1} in the nitrogen-bonding range.

Pending the acquisition of X-ray structure data it thus seems reasonable to assume that the 1:1 complexes prepared in this work also form double-chain structures. The CN stretching frequency shift from one complex to another might then be interpreted as indicating the relative Ag-N and Ag-S bond strengths within the double chain.

The 1:2 complexes prepared in this work probably all have dimeric structures involving a central $(AgSCN)_2$ ring with a quasiplanar structure. This prediction is based on conclusions from X-ray study on $AgSCN \cdot 2PPh_3$.[13] The bridging role of the thiocyanate group within the dimer is consistent with CS stretching vibration values and as with the 1:1 complexes the CN stretch values could be tentatively considered to reflect the relative Ag-N and Ag-S bond strengths.

It is of particular interest to note that complexes of both 1:1 and 1:2 stoichiometries were formed with diethylphenylphosphine. It will be noted further that the 1:1 complex has a CN stretching frequency that is 45 cm^{-1} greater than the 1:2 complex indicating a substantially greater relative sulfur bond strength in the 1:1 complex. The synthesis of these compounds seem to be at least a partial fulfillment of the prediction by Turco and Pecile,[4] that in compounds of the type $M(CNS)_mX_n$ a change in the m:n ratio might change the bonding mode of the thiocyanate group. This phenomenon of ligand-multiplicity linkage isomerism has apparently been observed previously with the complexes of bis(diphenylphosphino)acetylene with gold(I), $(DPPA)Au_2(SCN)_2$ (believed to be S bonded) and $(DPPA)_3Au_2(NCS)_2$ (believed to be N bonded).[14,15]

Table II. Infrared Data (cm^{-1})

Compd	ν(C-N)[a]	ν(C-S)[b]	δ(N-C-S)
$AgCNS \cdot PEt_2Ph$	2128 vs, 2075 sh	*c*	450 m, 441 m
$AgCNS \cdot P(i\text{-}Pr)_3$[d]	2111 s	738 m	475 s
$AgCNS \cdot P(n\text{-}Bu)_3$	2108 vs, 2068 sh	*c*	454 w, 444 w
$AgCNS \cdot PMe_3$	2100 s, 2050 sh	757 m	456 w, 447 w
$AgCNS \cdot 2PPh_3$	2092 vs, 2050 sh	*c*	484 m
$AgCNS \cdot 2PCy_3$[d]	2090 s	732 w	462 s
$AgCNS \cdot P(n\text{-}Pr)_3$[d]	2090 s	*c*	*c*
$AgCNS \cdot 2SbPh_3$	2084 vs	754 w	*c*
$AgCNS \cdot 2PEt_2Ph$	2083 s	*c*	494 m
$AgCNS \cdot 2AsPh_3$	2082 vs	*c*	478 m
$AgCNS \cdot 3PEtPh_2$	2074 vs	*c*	*c*

[a] M-SCN, $\gtrsim$2100; M-NCS, $\lesssim$2100; M-NCS-M, $\gtrsim$2140. [b] M-SCN, 690-720; M-NCS, 780-860; M-NCS-M, 720-780. [c] Masked by ligand absorptions. [d] C. Pecile, *et al., Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, 28, 189 (1960).

As previously mentioned the 1:3 stoichiometry observed with ethyldiphenylphosphine is somewhat surprising in view of the 1:2 stoichiometries observed with both diethylphenyl- and triphenylphosphine. With three ligands in addition to the thiocyanate group coordinated to the silver it is likely that this complex is a monomer and the low CN stretch value of 2074 cm^{-1} seems to be a definite indication of Ag-N bonding.

Registry No. $AgCNS \cdot PMe_3$, 38744-31-9; $AgCNS \cdot PBu_3$, 38744-32-0; $AgCNS \cdot PEt_3$, 38744-33-1; $AgCNS \cdot 2PEt_2Ph$, 38671-58-8; $AgCNS \cdot 3PPh_2Et$, 38731-29-2; $AgCNS \cdot 2PPh_3$, 36470-96-9; $AgCNS \cdot 2AsPh_3$, 38671-60-2; $AgCNS \cdot 2SbPh_3$, 38671-61-3.

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Absence of Selectivity in the Synthesis and Equilibration of $[Co(en)_2(S\text{-}glu)]^+$ Ions

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It has been reported[1,2] that treatment of an aqueous solution of racemic $[Co(en)_2CO_3]ClO_4$ with (*S*)-(+)-glutamic acid at elevated temperatures (steam bath or 100°) results in the initial formation of Λ-(+)$[Co(en)_2(S\text{-}glu)]^+$ followed by the slower formation of an equal amount[3] of the Δ-*S* dia-

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