

the purification of $[(\text{CH}_3\text{S})_2\text{Fe}(\text{CO})_2]_n$ was not possible owing to its insolubility. Upon heating above $\sim 110^\circ$, $[(\text{CH}_3\text{S})_2\text{Fe}(\text{CO})_2]_n$ gradually darkened without melting.

Anal. Calcd. for $n(\text{C}_4\text{H}_8\text{O}_2\text{S}_2\text{Fe})$: C, 23.3; H, 2.9; S, 31.0; Fe, 27.2; O, 15.5. Found: C, 23.3, 22.2; H, 3.1, 2.8; S, 31.0, 30.4; Fe, 26.6, 27.2; O, 15.8, 16.4.

Infrared Spectrum.²⁸—Metal carbonyl bands at 2010 (vs), 1966 (m), 1956 (s), and 1945 (m) cm^{-1} ; other bands at 1418 (w), 1297 (w), and 940 (w) cm^{-1} .

Preparation of $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_4\text{C}_7\text{H}_8$.—A mixture of 3.74 g. (10 mmoles) of $[\text{CH}_3\text{SFe}(\text{CO})_2]_2$ ($\sim 80\%$ *anti* and $\sim 20\%$ *syn*), 5.0 ml. (4.5 g., 49 mmoles) of bicycloheptadiene, and 50 ml. of thiophene-free benzene was refluxed 70 hr. with stirring under nitrogen. Solvent was removed from the filtered reaction mixture at $\sim 25^\circ$ (35 mm.) leaving a dark red residue. After admitting nitrogen, the residue was extracted with 70 ml. of pentane in four portions and the filtered pentane extracts were chromatographed on a 2×50 cm. alumina column. The chromatogram was developed with pentane. The first two red to red-orange bands were eluted with pentane. Evaporation of the filtered eluates from these two bands gave 1.26 g. of *anti*- $[\text{CH}_3\text{SFe}(\text{CO})_2]_2$ and 0.15 g. of *syn*- $[\text{CH}_3\text{SFe}(\text{CO})_2]_2$, respectively; total recovery of both $[\text{CH}_3\text{SFe}(\text{CO})_2]_2$ isomers, 1.41 g. (38%).

After removing both isomers of $[\text{CH}_3\text{SFe}(\text{CO})_2]_2$ from the chromatography column, a brown band remained. This band was eluted with pentane. The dark brown pentane eluate (volume ~ 250 ml.) was filtered by gravity, collecting the filtrate under nitrogen. Removal of solvent ($\sim 25^\circ$ (35 mm.)) from this filtrate left a brown liquid. This liquid was extracted with ~ 50 ml. of pentane in three portions. The filtered pentane extracts were concentrated to ~ 30 ml. and then cooled in a -78° bath. Separation of the dark brown crystalline product was slow and it was therefore advisable to keep the pentane solution at -78° for at least 40 hr. before filtering the product. After filtration and drying in the usual manner, 0.62 g. (15% conversion, 24% yield) of dark brown crystalline $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_4\text{C}_7\text{H}_8$, m.p. $84-86^\circ$, was obtained.

Attempts to accelerate this reaction by carrying it out in boiling toluene or xylene rather than boiling benzene gave little or none of the desired product.

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{S}_2\text{Fe}_2$: C, 38.1; H, 3.4; S, 15.6; O, 15.6; Fe, 27.3; mol. wt., 410. Found: C, 37.9, 37.7; H, 3.4, 3.3; S, 16.1, 15.3; O, 16.0, 16.5; Fe, 27.1, 26.9; mol. wt., 400.

Infrared Spectrum.²⁸—Carbon-hydrogen stretching frequencies at 2910 (vw) and 2875 (vw) cm^{-1} ; metal carbonyl bands at 2040 (s), 2029 (m), 1974 (s), 1963 (s), and 1943 (m) cm^{-1} ; other bands at 1417 (w), 1404 (w), 1300 (w), 1243 (vw), 1177 (w), 1154 (vw), 1077 (w), 1032 (vw), 992 (vw), 947 (w), 942 (w), 893 (vw), 856 (vw), 800 (vw), 777 (w), 745 (vw), 730 (vw), 728 (vw), 697 (vw), and 685 (vw) cm^{-1} .

Proton N.m.r. Spectrum.—(a) (CS_2 solution): Resonances at τ 6.39 (apparent triplet), 6.73 (apparent doublet), 8.80 (apparent singlet), and 8.98 (apparent singlet) of approximate relative intensities 4:2:5:3. (b) (C_6H_6 solution): Resonances at τ 6.80 (unclearly resolved), 7.14 (broad unresolved), 8.89 (sharp singlet), 9.26 (unresolved singlet), and 9.40 (sharp singlet) of approximate relative intensities 4:2:3:2:3. (c) (C_6F_6 solution): Resonances at τ 6.30 (complex with at least five discernible peaks), 6.58 (complex with at least four discernible peaks), 8.73 (unresolved singlet), 8.82 (sharp singlet), and 8.89 (sharp singlet) of approximate relative intensities 4:2:2:3:3.

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(23) The metal carbonyl region of this spectrum was studied in a halocarbon oil mull on a Beckman IR-9 double beam spectrometer with grating optics. The remainder of the spectrum is reported as obtained from a potassium bromide pellet on a Perkin-Elmer Model 21 double beam spectrometer.

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Infrared Spectra of Substituted Thiocyanate Complexes. The Effect of the Substituent on Bond Type. I

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Metal-thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanate group is bonded to the metal through the nitrogen atom (M-NCS), through the sulfur atom (M-SCN), or through both by means of bridging (M-NCS-M).¹ It has been found that metals classified by Ahrlund, Chatt, and Davies² as class a are generally bonded to the nitrogen atom, whereas class b metals are bonded to the sulfur atom.

Turco and Pecile,³ investigating compounds of the type $[\text{ML}_2(\text{NCS})_2]$ with $\text{M} = \text{Pd}$ or Pt , found that when L is an amine or a thiocyanate ion, the thiocyanate group is S-bonded, but when L is a trialkylphosphine the thiocyanate group is N-bonded. They suggested that, though the sulfur atom is a weaker σ donor than the nitrogen atom, M-S bonding is stabilized by π back bonding from metal to sulfur and that when L is a strong π acceptor, as for example triethylphosphine, the M-S π bond is so reduced in strength that the N-bonded isomer becomes the more stable one.

Burmeister and Basolo^{4,5} widened the study of these compounds to include other organic ligands and were able to isolate both N- and S-bonded isomers of $[\text{Pd}(\text{As}(\text{C}_6\text{H}_5)_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{dipy})(\text{NCS})_2]$ by suitable adjustment of the conditions of preparation.

The criterion adopted until now to establish the bond type is that a C-S stretching frequency of 780-860 cm^{-1} is indicative of N-bonding, while a frequency of ca. 700 cm^{-1} indicates S-bonding. It had previously been noted that the NCS deformation mode can be used to characterize the bond type,^{1b,6} being a single band at 460-490 cm^{-1} for N-thiocyanates and a band at 410-440 cm^{-1} , with weaker satellites at higher frequencies, for S-thiocyanates. Furthermore the first overtone of the NCS deformation mode has an intensity comparable to that of the C-S stretching mode⁷: its value in S-thiocyanato complexes lies between 800 and 880 cm^{-1} so that it may be erroneously assigned as the C-S stretching band of an N-thiocyanato complex.

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TABLE I

VIBRATION FREQUENCIES (CM.⁻¹) OF THIOCYANATE GROUP IN [PdL₂(SCN)₂] AND [PtL₂(SCN)₂] COMPLEXES

Complex	C-N str.	C-S str.	N-C-S bend.	Bend. overtone
[Ni(P(<i>n</i> -C ₄ H ₉) ₃) ₂ (NCS) ₂]	2090 s, br; 2050 sh	864 s	453 w, 445 sh	<i>a</i>
[Ni(P(C ₆ H ₅) ₃) ₂ (NCS) ₂]	2078 s, br	868 m	458 w	
[Pd(P(C ₆ H ₅) ₃) ₂ (NCS) ₂]	2095 s, br	853 m	<i>a</i>	
[Pd(P(<i>n</i> -C ₄ H ₉) ₃) ₂ (NCS) ₂]	2100 s, br	846 ms	448 m	<i>a</i>
[Pd(As(C ₆ H ₅) ₃) ₂ (NCS) ₂]	2085 s, br	854 m	<i>a</i>	930 vw; 920 vw
[Pd(As(<i>n</i> -C ₄ H ₉) ₃) ₂ (SCN) ₂]	2115 s, sp	<i>a</i>	452 m; 422 m	846 vw
[Pd(As(C ₆ H ₅) ₃) ₂ (SCN) ₂]	2120 s, sp	<i>a</i>	418 vw	834 vw
[Pd(Sb(C ₆ H ₅) ₃) ₂ (SCN) ₂] ^b	2119 sh; 2115 s, sp	<i>a</i>		<i>a</i>
[Pd(phen)(SCN) ₂]	2116 s, sp	697 w	460 mw; 418 m	<i>a</i>
[Pd(bipy)(SCN) ₂] ^b	2117 s, sp; 2108 s, sp	700 w		
[Pd(bipy)(NCS) ₂]	2100 s, br	845 m	458 w	920 w
[Pd(5-nitrophen)(NCS) ₂]	2090 s, br	<i>a</i>	458 w	
[Pd(py) ₂ (SCN) ₂]	2112 s, sp	<i>a</i>	424 w; (436 s?)	
<i>trans</i> -[Pt(py) ₂ (SCN) ₂]	2115 s, sp	<i>a</i>	426 mw; 418 sh	855 w
<i>cis</i> -[Pt(py) ₂ (SCN) ₂]	2120 s, sp	<i>a</i>	480 w, 465 mw 430 sh; 425 m	848 w

^a Band masked by the absorption of the organic ligand. ^b Frequencies taken from ref. 5. Abbreviations: py, pyridine; bipy, 2,2'-bipyridine; phen, 1,10-phenanthroline; s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder.

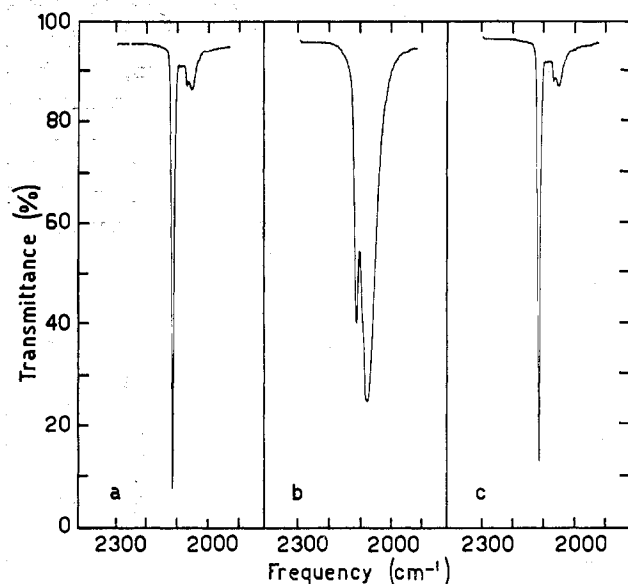


Figure 1.—C-N stretching absorption band of (a) solid, (b) fused, and (c) solidified [Pd(As(*n*-C₄H₉)₃)₂(SCN)₂].

We have therefore extended the investigation of the compounds [ML₂(NCS)₂] to include the infrared region 800–400 cm.⁻¹. The assignments of the bands due to the thiocyanate groups were made by comparing the spectra with those of the analogous halo complexes. The results are given in Table I.

The NCS bending vibration gives rise to an absorption band at 450 cm.⁻¹ in some compounds. As this frequency is intermediate between those usually observed in thio- and isothiocyanate complexes, the spectra were compared with those of the analogous nickel complexes. The latter are generally held to be N-bonded, and X-ray powder photographs showed them to be isomorphous with the palladium complexes. As the NCS bending band in [Ni(P(*n*-C₄H₉)₃)₂(NCS)₂] appears at 453 cm.⁻¹ and in the palladium analog at 448 cm.⁻¹, it is concluded that the NCS bending frequency may fall as low as 450 cm.⁻¹ in N-thiocyanato

complexes. The conclusions of Turco and Pecile concerning the bond type are also confirmed.

In the spectrum of the complex [Pd(As(*n*-C₄H₉)₃)₂(SCN)₂] bands are found at 846, 452, and 422 cm.⁻¹, and the sharp C-N stretching band at 2115 cm.⁻¹ indicates Pd-S bonding. When the compound melts a broad and intense band appears at 2085 cm.⁻¹ and at the same time the intensity of the 2115 cm.⁻¹ band decreases (see Figure 1). These results show that the process of fusion is accompanied by a partial isomerization and formation of the N- isomer; on cooling the melt the S- isomer alone crystallizes out of the melt. The band at 845 cm.⁻¹ is therefore assigned as the first overtone of the NCS bend fundamental found at 422 cm.⁻¹. Similarly the bands at 848 and 855 cm.⁻¹ in *cis*- and *trans*-[Pt(py)₂(SCN)₂] are assigned as harmonics of the deformation frequencies found at 425 and 426 cm.⁻¹. The NCS bending frequency of [Pd(py)₂(SCN)₂] is found at 424 cm.⁻¹.

The infrared spectra of the three pyridine complexes all indicate metal to sulfur bonding; there is no ambiguity involved in the assignments for the other compounds. The most reliable feature for diagnosing bond type in the complexes [PdL₂(SCN)₂] is shown by this study to be the C-N stretching band: it is sharp and above 2000 cm.⁻¹ in the S-bonded complexes and broad and below 2000 cm.⁻¹ in the N-bonded complexes.

It has also been shown that when the organic ligand is a phosphine the thiocyanate group is bonded through the nitrogen atom, when the ligand is triphenylarsine both N- and S- isomers are possible, and when it is tributylarsine only the S-bonded compound is obtained.

According to the suggestion made by Turco and Pecile,³ this behavior can be explained by ordering the π -acceptor capacity of the ligand L toward palladium in the following manner: stibine < arsine < phosphine; the availability of palladium d electrons for the Pd-S π bonding varies in the opposite order. Thus, with phosphines the bonding is determined by the relative σ -bond strengths, and the Pd-N bond is more stable.

With triphenylarsine sufficient Pd-S π bonding is possible to make the S- isomer also preparable. Tributylarsine, which should be a slightly weaker π acceptor than triphenylarsine, gives only the S- isomer in the solid state, though on fusion the N- isomer also forms.

In the series of compounds where the donor atom is an aromatic nitrogen atom, 5-nitro-*o*-phenanthroline gives the N- isomer whereas pyridine and *o*-phenanthroline give the S- isomer. Intermediate between these two is the ligand dipyridyl which gives both linkage isomers.

Experimental

The compounds were prepared by the procedure of Burmeister and Basolo⁵ and analyzed satisfactorily for nitrogen. The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer Model 337 spectrophotometer.

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The Standard Oxidation Potentials of the Silver-Silver Cobalticyanide and Mercury-Mercurous Cobalticyanide Electrodes at 25°

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There are few thermodynamic data available on cobalticyanide salts.¹⁻³ The solubility product of $\text{Ag}_3\text{Co}(\text{CN})_6$ obtained from potentiometric titration data¹ of a cell with liquid junctions is too large to be consistent with the chemical behavior of this salt. It has been found in this investigation that the solubility product for $\text{Ag}_3\text{Co}(\text{CN})_6(\text{s})$ obtained from cells free from liquid junctions is much smaller than the previously reported value.

Experimental

Reagents.—J. T. Baker reagent grade KCl was used without further purification. The $\text{K}_3\text{Co}(\text{CN})_6$ was obtained from G. F. Smith Chemical Co. The impure salt was recrystallized four times from distilled water, the hot (60°) concentrated solution being filtered each time. The mercury (triple distilled, purity exceeds A.C.S. specifications) was obtained from Bethlehem Apparatus Co. Samples of $\text{Ag}_3\text{Co}(\text{CN})_6$ and $(\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ were obtained by adding slowly with continuous stirring a 0.1 M solution of $\text{K}_3\text{Co}(\text{CN})_6$ to a hot (50–60°) acidified 0.1 M

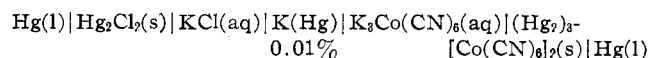
solution of reagent grade AgNO_3 and $\text{Hg}_2(\text{NO}_3)_2$ (in 10% excess), respectively. The precipitates were washed by repeated decantation with distilled water until tests for metal ions proved negative and then air-dried in the dark.

*Anal.*⁴ Calcd. for $\text{Ag}_3\text{Co}(\text{CN})_6$: C, 13.37; N, 15.60. Found: C, 13.45; N, 15.57. Calcd. for $(\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$: C, 8.45; H, 0.47; N, 9.85. Found: C, 8.44; H, 0.40; N, 9.85. Calcd. for $\text{K}_3\text{Co}(\text{CN})_6$: C, 21.68; N, 25.29. Found: C, 21.52; N, 25.35.

Electrical Cell Measurements.—Voltages were measured with a Leeds and Northrup Type K-3 certified potentiometer and a Leeds and Northrup No. 2430C galvanometer. The voltage standard was an Eppley Laboratory unsaturated Weston cell (certified June 1964). Electrode compartments were similar to those described by Hills and Ives,⁵ and the calomel electrodes were set up according to their prescription. The insides of the electrode compartments were silicone-coated.⁵ The cell leads were brought in through a capillary to the base of the compartment and sealed in place with paraffin wax. These leads were of platinum and were completely covered with mercury. The silver electrode was a piece of Englehard Industries No. 24 B. and S. gauge silver wire bent in a loop so that the end was beneath the wax surface. This silver loop was electroplated in place by rapid electrolysis of a silver nitrate solution. A new silver electrode was prepared for each cell measurement. Air was excluded from all cells by a stream of purified nitrogen from a presaturator filled with cell electrolyte. Light was excluded from the silver-silver cobalticyanide and mercury-mercurous cobalticyanide electrodes by wrapping the electrode compartments in aluminum foil. The solid phases in these electrodes were white at the completion of the measurements. The cells were kept at $25.0 \pm 0.005^\circ$ in a grounded water bath. The amalgam junction connector used has been described.⁶ The dilute (0.01 wt. % K) potassium amalgam was prepared by electrolysis of 2 M KOH with a mercury cathode and dried on the vacuum line.

Results

Mercurous Cobalticyanide.—The potential of the mercury-mercurous cobalticyanide electrode was determined in the cell



Because of a side reaction between the K(Hg) and the $\text{K}_3\text{Co}(\text{CN})_6$ solution (color changes from very pale to deep yellow in the vicinity of the K(Hg) the cell was allowed to equilibrate overnight with pure mercury in the connector. The mercury was then displaced with 0.01% K(Hg) and stable voltages could be obtained for 2–3 hr. if the $\text{K}_3\text{Co}(\text{CN})_6$ in contact with the K(Hg) was occasionally renewed. If left to stand overnight in contact with K(Hg) the $\text{K}_3\text{Co}(\text{CN})_6$ solution became a deep yellow in color and the mercurous cobalticyanide solid phase was no longer present.

At 0.125 m KCl and 0.128 m $\text{K}_3\text{Co}(\text{CN})_6$ the observed cell voltage was (calomel negative) 117 ± 0.5 mv., and at 0.150 m KCl and 0.0500 m $\text{K}_3\text{Co}(\text{CN})_6$ it was 159 ± 0.5 mv. Application of the Nernst equation to the cell reaction yields at 25° $(\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2(\text{s}) + 6\text{KCl}(\text{aq}) = 3\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{K}_3\text{Co}(\text{CN})_6(\text{aq})$, $E = E_1^\circ - E_2^\circ - 0.07888 \log 27^{1/4} m \gamma_{\pm} + 0.11832 \log m' \gamma_{\pm}'$. E_1° is the standard oxidation potential of the

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