this band (due to transitions between the $d_{x^2-y^2}$, d_{xy} orbitals and the d_{z^2} orbital) may reflect the extent of metal-to-ligand π back bonding between the $d_{x^2-y^2}$, d_{xy} orbitals of the metal and the empty d orbitals of the sulfur. If this is so, the π-bonding character of the Ni–S bond appears to remain approximately constant throughout this series and to be substantially less than that of the Ni–As bond in the corresponding QAS complexes (Figure 3).

The intensity of the higher-energy band varies rather systematically whenever the fifth ligand is Cl, Br, I, NCS, etu, and tu (ϵ 250–1015), but it is considerably greater whenever L = $P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$ ($\epsilon \sim$12,000). The data suggest that the higher-energy band may be sensitive to the π-bonding nature of the two ligands in the apical positions of the trigonal bipyramid. Further studies are in progress to test these observations.

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Thiocyanatocarbonyl Complexes of Manganese(I)[1]

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A series of thiocyanatocarbonyl complexes of manganese(I) was prepared by reaction of thiocyanatopentacarbonylmanganese(I) with neutral ligands L, where L is an amine, phosphine, arsine, or stibine, and/or by metathesis involving analogous chloro or bromo complexes and potassium thiocyanate. The infrared spectra suggest that the tetracarbonyls, $Mn(CO)_4L(SCN)$, are sulfur-bonded in the solid phase and chloroform solutions, whereas the *trans* and *cis* tricarbonyls, $Mn(CO)_3L_2(CNS)$, are nitrogen-bonded, the apparent exceptions being *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$ and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$. A possible explanation of these modes of manganese–thiocyanate attachment is offered in terms of Mn=C=O π bonding. Some unusual spectral features of the nitrogen-bonded *cis* tricarbonyls are also presented and interpreted on the basis of the proposed bonding hypothesis. It is suggested that steric factors play a major role in stabilizing manganese–sulfur linkage in the *cis* tricarbonyls containing triphenylarsine and -stibine. Finally, metal–thiocyanate bonding in six-coordinate manganese(I) carbonyls is compared with that in four-coordinate palladium(II) complexes.

Introduction

Recently, we have reported the synthesis of thiocyanatopentacarbonylmanganese(I),[3] which represents the first simple thiocyanato metal carbonyl. Infrared spectral studies on this complex suggested that equilibria between the linkage isomers are established in several solvents and that the S- and N-bonded species prevail in the solid phase and acetonitrile, respectively. Because of a facile interconversion of the two linkage forms of $Mn(CO)_5CNS$,[4] it was of interest to investigate the effect of partial replacement of the carbonyl groups by various neutral ligands on the mode of manganese–thiocyanate attachment in the resultant derivatives.

That the nature of other ligands in a complex can strikingly influence the bonding of a coordinated thiocyanate has been clearly demonstrated for palladium(II) and platinum(II) square-planar compounds by Turco and Pecile[5] and, more recently, by Burmeister and Basolo.[6] The latter authors suggest that a delicate balance of both electronic and steric factors is responsible for the observed variations in the mode of metal–thiocyanate attachment.

Unlike the four-coordinate complexes above, "octahedral" thiocyanato compounds have not yet been systematically studied with respect to the bonding. This may be due, at least in part, to a greater stereochemical complexity of six-coordinate compounds. Indeed, a thorough study of metal–thiocyanate bonding requires synthesis of a number of representative complexes and a complete knowledge of their structures. Such information is frequently not available.

The above difficulty could be conceivably avoided in the investigation of thiocyanatomanganese(I) carbonyl complexes. By analogy with the halogenopentacarbonyls, $Mn(CO)_5CNS$ is expected to undergo substitution reactions with a variety of neutral[7] and negatively-charged[8] ligands. For $Mn(CO)_5X$ (X = Cl, Br, I), these reactions are generally highly stereospecific, and the structures of the products can be often elucidated by infrared spectroscopy. Therefore, derivatives of $Mn(CO)_5CNS$ offer a systematic approach to the study of various effects that the nature and position of different ligands in the complex exert on the mode of manganese–thiocyanate attachment.

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5–10, 1964, and at the Eighth International Conference on Coordination Chemistry, Vienna, Austria, Sept. 7–11, 1964.

[2] Based on the Ph.D. thesis submitted by M. F. F. to The Ohio State University, Aug. 1964.

[3] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 857 (1965).

[4] The symbols NCS and SCN designate N- and S-bonding, respectively; CNS denotes that either the bonding is not known or both isomers are present in equilibrium.

[5] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

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

[7] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 2215 (1963), and references therein.

[8] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 434 (1964); also, R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).

TABLE I

SYNTHETIC PROCEDURES, REACTION TEMPERATURES AND TIMES, METHODS OF PURIFICATION, PER CENT YIELDS, AND ANALYTICAL DATA FOR THE THIOCYANATO MANGANESE(I) CARBONYL COMPLEXES

		Reaction				Analyses, %					
						Calcd.			Found		
Complex	Synthetic procedure[a]	temp., °C.	time, hr.	Method of purification[b]	Yield, %	C	H	S or N	C	H	S or N
cis-$Mn(CO)_3(py)_2NCS$	A	25	12	Y ($CHCl_3$)	95–100	47.34	2.84	S, 9.03	46.99	2.79	S, 8.81
	B	50	8		70						
cis-$Mn(CO)_3(bipy)NCS$	A	25	12	Y (CH_2Cl_2)	95–100	47.60	2.28	S, 9.08	47.82	2.42	S, 8.89
	B	50	8		70						
cis-$Mn(CO)_3(p\text{-tol})_2NCS$	A	25	12	U	95–100	52.56	4.41	S, 7.79	52.9	4.63	S, 7.50
cis-$Mn(CO)_3(\gamma\text{-pic})_2NCS$	A	25	12	X ($CHCl_3$)	Not det.	50.13	3.68	N, 10.96	49.98	3.74	N, 10.85
	B	60	8		60						
cis-$Mn(CO)_3(p\text{-can})_2NCS$	A	25	12	W ($CHCl_3$–CH_3CN, 50:50, volume)	Not det.	42.49	2.67		42.18	2.44	
	B	60	8		65						
cis-$Mn(CO)_3(p\text{-fan})_2NCS$	A	25	12	W ($CHCl_3$–CH_3CN, 50:50, volume)	Not det.	45.83	2.88		45.55	2.79	
	B	60	8		60						
trans-$Mn(CO)_3[P(C_6H_5)_3]_2NCS$	A	25	12	Z (CH_2Cl_2)[c]	95	66.57	4.19	N, 1.94	66.7	4.36	N, 1.79
	B	50	8		75						
$Mn(CO)_4[P(C_6H_5)_3]SCN$	A[d]	25	24	X (C_6H_6)	8			N, 2.87			N, 2.79
trans-$Mn(CO)_3[As(C_6H_5)_3]_2NCS$	A	80	12	Y (CH_2Cl_2)[c]	50	59.35	3.74	N, 1.73	60.8	4.24	N, 1.75
cis-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$[e]	A	25	12	U	60–70	59.35	3.74	N, 1.73	55.4	3.70	N, 2.54
$Mn(CO)_4[As(C_6H_5)_3]SCN$	A[d]	25	24	X (C_6H_6)	48	52.00	2.85	N, 2.64	52.2	3.03	N, 2.71
	B	50	8		40						
trans-$Mn(CO)_3[Sb(C_6H_5)_3]_2NCS$	A	80	12	Y (CH_2Cl_2)[c]	79	53.19	3.35	N, 1.55	53.09	3.41	N, 1.48
cis-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$	A	25	12	U	95	53.19	3.35	N, 1.55	52.7	3.7	N, 1.59
$Mn(CO)_4[Sb(C_6H_5)_3]SCN$[f]	A[d]	25	24	Y (C_6H_6)	5						
cis-$Mn(CO)_3(diphos)NCS$	A	25	12	U	95–100	60.34	4.06	N, 2.35	59.95	4.54	N, 2.30

[a] Procedure A = $Mn(CO)_5SCN$ + excess (*ca.* 5:1) ligand; B = corresponding chloro or bromo complex + excess (*ca.* 10:1) KSCN. [b] U = crystallization from chloroform–petroleum ether; W = chromatography on Florisil; X = chromatography on acid alumina; Y = chromatography on neutral alumina; Z = chromatography on basic alumina. Eluents are enclosed by parentheses; in all cases, except as specified, the product is cleanly eluted first as a yellow band. [c] The tetracarbonyl is eluted first with benzene. [d] Equimolar amounts of $Mn(CO)_5SCN$ and ligand. [e] Contains a substantial amount of the tetracarbonyl, which is difficult to remove. [f] Small yields prevented elemental analyses; characterized on the basis of the infrared spectrum, which is very similar to that of $Mn(CO)_4[As(C_6H_5)_3]SCN$. Abbreviations: py, pyridine; bipy, 2,2′-bipyridine; *p*-tol, *p*-toluidine; γ-pic, 4-methylpyridine; *p*-can, *p*-chloroaniline; *p*-fan, *p*-fluoroaniline; diphos, 1,2-bis(diphenylphosphino)ethane. NCS and SCN designate Mn–NCS and Mn–SCN bonding, respectively.

Reported now is the preparation of several substituted thiocyanatomanganese(I) carbonyl compounds as well as the infrared spectral investigation of their structures, with particular emphasis on the bonding of the metal and thiocyanate.

Experimental

Materials.—Using dimanganese decacarbonyl, kindly donated by Professor H. B. Gray of Columbia University and Dr. J. A. Ibers of the Brookhaven National Laboratory, the complexes $Mn(CO)_5Cl$,[9] $Mn(CO)_5Br$,[9] and $Mn(CO)_5SCN$[3] were prepared as described in the literature. 1,2-Bis(diphenylphosphino)ethane was synthesized by the method of Chatt and Hart.[10]

p-Toluidine, 4-methylpyridine, *p*-chloroaniline, and triphenylarsine were purchased from Eastman Organic Chemicals, whereas 2,2′-bipyridine, *p*-fluoroaniline, triphenylphosphine, and triphenylstibine were obtained from Matheson Coleman and Bell. All of these compounds were reagent grade.

Acetonitrile was purified as described earlier.[3] The other solvents, except low boiling (30–60°) petroleum ether, were analytical reagent grade.

Chromatographic grade acidic, neutral, and basic alumina (Camag) were purchased from Arthur H. Thomas Co. Florisil (60/100 mesh) was obtained from Floridin Co., Tallahassee, Fla.

The complex $Mn(CO)_4[As(C_6H_5)_3]Cl$ was prepared by the method of Angelici and Basolo.[11] Other halogenocarbonyl compounds,[12] *i.e.*, *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Cl$, *cis*-$Mn(CO)_3(C_5H_5N)_2Cl$, and *cis*-$Mn(CO)_3L_2Br$[13] (L = 4-methylpyridine, *p*-chloroaniline, *p*-fluoroaniline; L_2 = 2,2′-bipyridine) were prepared by the following general method. The pentacarbonyl halide (*ca.* 1 mmole) and ligand (2–5 mmoles) in chloroform (10–15 ml.) were allowed to react for 12 hr. at 25°. The mixture was then filtered and the solvent evaporated to dryness in a stream of nitrogen. The resultant derivatives can be purified by crystallization from chloroform–petroleum ether. They were not characterized beyond infrared spectral measurements.

Synthesis of Substituted Thiocyanatomanganese(I) Carbonyl Complexes. *cis*-$Mn(CO)_3(C_5H_5N)_2NCS$. (a) From $Mn(CO)_5SCN$ and Pyridine.—Pyridine (0.1 ml., *ca.* 1.2 mmoles) in 5 ml. of chloroform was added to 0.05 g. (0.2 mmole) of $Mn(CO)_5SCN$ in a test tube protected from light with masking tape. Immediately, a slow evolution of carbon monoxide ensued. The reaction was allowed to proceed for 12 hr. at 25°, after which time the mixture was filtered and the solvent and excess pyridine were evaporated in a stream of nitrogen. The resultant solid was dissolved in 2 ml. of chloroform and chromatographed on a neutral alumina column (30 × 2 cm.) using chloroform eluent. The yellow band was collected and the solvent evaporated [25° (~20 mm.)] to give 0.07 g. (*ca.* 100%) of the product. The analytical data are given in Table I.

(b) By Metathesis.—Potassium thiocyanate (1 g., ~10 mmoles) in 4 ml. of water was added to $Mn(CO)_3(C_5H_5N)_2Cl$ (0.33 g., 1 mmole) dissolved in 30 ml. of methanol. The re-

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(9) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(10) J. Chatt and J. Hart, *ibid.*, 1378 (1960).

(11) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).

(12) *cis* and *trans* refer to mutual positions of the two neutral ligands other than CO. These are *cis* to thiocyanate in both forms.

(13) The derivatives with L = 4-methylpyridine, *p*-chloroaniline, and *p*-fluoroaniline are new compounds.

Table II

CN and CO Stretching Frequencies (cm.$^{-1}$) of $Mn(CO)_4L(SCN)$ Complexes in Chloroform[a]

Complex	CN stretch (SCN)	CO stretches (3A′ + A″)
$Mn(CO)_4[P(C_6H_5)_3]SCN$	2151 m	2097 w, 2045 s, 1963 s, 1927 s
$Mn(CO)_4[As(C_6H_5)_3]SCN$	2149 m	2093 w, 2037 s, 1960 s, 1931 s
$Mn(CO)_4[Sb(C_6H_5)_3]SCN$	2156 m	2099 w, 2046 s, 1962 s, 1938 s

[a] Abbreviations: s, strong; m, medium; w, weak.

action mixture was stirred under nitrogen for 8 hr. at 50°. The solvent was then removed [50° (~20 mm.)] and the residue extracted with 8 ml. of chloroform. The mixture was filtered and the volume of the filtrate reduced to *ca.* 3 ml. in a stream of nitrogen. Purification was effected by chromatography, as described above, the unreacted chloro complex remaining on the column. The infrared spectrum of this sample exactly matched that of the product from $Mn(CO)_5SCN$ and pyridine.

Other Complexes.—The other complexes were prepared by analogous methods. Synthetic procedures, reaction times and temperatures, methods of purification, yields, and chemical analyses are summarized in Table I.

All thiocyanatocarbonyl complexes obtained from metathetical reactions can be effectively purified by chromatography and are eluted first, before the corresponding unreacted chloro or bromo derivatives.

Reactions of $Mn(CO)_5CNS$ with triphenylphosphine, -arsine, and -stibine (L) give mixtures of three products (two with $P(C_6H_5)_3$), *i.e.*, $Mn(CO)_4L(SCN)$, *cis*-$Mn(CO)_3L_2(SCN)$, and *trans*-$Mn(CO)_3L_2(NCS)$. The yield of each complex depends on the relative amount of ligand used and on the reaction time and temperature (Table I). The tetracarbonyls may be readily separated from the *trans* tricarbonyls by chromatography; however, the *cis* tricarbonyls could not be eluted from the column and, therefore, were purified by crystallization. Because of similar solubility properties of $Mn(CO)_4L(SCN)$ and *cis*-$Mn(CO)_3L_2(SCN)$, the latter could not be obtained pure in large yields; this is reflected in some chemical analyses shown in Table I. Repeated crystallizations from chloroform–petroleum ether did, however, afford small quantities of pure *cis* tricarbonyls, the infrared spectra of which are consistent with the assigned structures.

Properties of the Complexes.—All of the derivatives are yellow solids, stable in air. The isothiocyanates can be readily recrystallized from chloroform–petroleum ether; the thiocyanates crystallize with difficulty and tend to form oils. Both are soluble in polar organic solvents such as dichloromethane, acetonitrile, and methanol. The molar conductivities of *cis*-$Mn(CO)_3L_2(NCS)$ (L = pyridine, 4-methylpyridine, *p*-chloroaniline, *p*-fluoroaniline; L_2 = 2,2′-bipyridine) and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2NCS$ in nitromethane (*ca.* 10^{-3} *M* solutions) are all less than 1 ohm^{-1} cm.^{2}.

Reaction of *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ with 2,2′-Bipyridine.—2,2′-Bipyridine (0.03 g., 0.2 mmole) and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ (0.09 g., 0.1 mmole) in 15 ml. of chloroform were heated for 6 hr. at 50°. The mixture was filtered and the solution evaporated to dryness in a stream of nitrogen. After washing with petroleum ether (5 × 20 ml.), the yellow solid was dissolved in chloroform (2 ml.) and chromatographed on a neutral alumina column using chloroform eluent. Evaporation of the solvent afforded 0.03 g. (*ca.* 90%) of *cis*-$Mn(CO)_3(bipy)NCS$, identified by its infrared spectrum.

Reaction of $Mn(CO)_5NCS$ with Triphenylstibine in Acetonitrile.—Triphenylstibine (0.35 g., 1 mmole) was added to $Mn(CO)_5NCS$ (0.05 g., 0.2 mmole) in 5 ml. of acetonitrile after the S-bonded carbonyl complex had completely rearranged to its linkage isomer. The reaction was allowed to proceed for 12 hr. at 25°, the mixture was filtered, and the volume of the solution was reduced to about 0.5 ml. in a stream of nitrogen. Addition of petroleum ether (50 ml.) afforded a yellow solid, which was collected on a filter and dried. The infrared spectrum revealed that the predominant product (60–80%) was *trans*-$Mn(CO)_3[Sb(C_6H_5)_3]_2NCS$, with a smaller amount (20–40%) of *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ also present.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer. A polystyrene standard was used for calibration in all cases. Solutions were placed in a 0.1-mm. NaCl cell, a variable thickness reference cell being used whenever necessary. Solids were examined in the form of Nujol mulls or thin films.[3]

Electrical Conductivity.—Measurements were made with an Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes.

Analyses.—The microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by A. Bernhardt Microanalytical Laboratories of the Max Planck Institute, Mulheim, Germany.

Results

Infrared Spectra and Structures of the Compounds.—The thiocyanatocarbonyl complexes of manganese(I) reported in this paper may be classified according to the composition and stereochemistry into three groups: the *cis* tetracarbonyls, the *cis* tricarbonyls, and the *trans* tricarbonyls. The structural assignments were made by comparing the intensities and positions of the observed carbonyl stretching frequencies with those predicted on simple group theoretical and symmetry grounds.[14] The proposed manganese–thiocyanate attachments are based on the frequencies of the CS stretching mode[5,15]; in some cases, additional support is derived from inspection of the CN stretching frequencies.[16] The positions of the former were determined by comparing the spectra in the 660–860 cm.$^{-1}$ range of the thiocyanato derivatives with those of the analogous chloro or bromo complexes.

The infrared absorptions of the tetracarbonyls in the 1900–2200 cm.$^{-1}$ range are listed in Table II. The number of carbonyl peaks and their relative intensities support the *cis* structure of each complex. No bands due to the CS stretching mode are discernible in the 780–860 cm.$^{-1}$ range even for concentrated mull suspensions of the tetracarbonyls; in the 680–720 cm.$^{-1}$ region, strong phenyl ring absorptions preclude possible detection of the carbon–sulfur peaks, which are generally weak in intensity.[5,6] It is therefore inferred that the thiocyanate is S-bonded in these derivatives.

Additional supporting evidence for S-bonding is obtained upon inspection of the CN stretching frequencies of the complexes. The bands at 2149–2156 cm.$^{-1}$ suggest that the SCN^- is attached *via* the sulfur atom; isothiocyanates usually absorb at lower frequencies (2100 cm.$^{-1}$ and below).[16] However, the

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(14) For a comprehensive discussion of applications of group theoretical methods to structural problems involving metal carbonyls see F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references therein.

(15) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(16) See P. C. H. Mitchell and R. J. P. Williams, *ibid.*, 1912 (1960).

TABLE III

CN, CO, AND CS STRETCHING FREQUENCIES (CM.$^{-1}$) OF *cis*-[$Mn(CO)_3L_2(CNS)$] COMPLEXES

Complex	CN stretch[a] (SCN)	CO stretches[a] (2A′ + A″)	CS stretch[b] (SCN)
$Mn(CO)_3(py)_2NCS$	2097 m	2039 s, 1954 s, 1924 s	813 m
$Mn(CO)_3(bipy)NCS$	2107 m	2038 s, 1951 s, 1941 s	813 m
$Mn(CO)_3(\gamma\text{-pic})_2NCS$	2097 m	2039 s, 1953 s, 1922 s	. . .[c]
$Mn(CO)_3(p\text{-tol})_2NCS$	2142 m	2036 s, 1954 s, 1942 s	800 m
$Mn(CO)_3(p\text{-can})_2NCS$	2142 m	2039 s, 1953 s, 1948 s	800 m
$Mn(CO)_3(p\text{-fan})_2NCS$	2142 m	2039 s, 1952 s, 1946 s	803 m
$Mn(CO)_3(diphos)NCS$	2110 m	2033 s, 1965 s, 1930 s	818 m
$Mn(CO)_3[As(C_6H_5)_3]_2SCN$	2148 m	2030 s, 1957 s, 1931 s	. . .[d]
$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$	2148 m	2030 s, 1955 s, 1930 s	. . .[d]

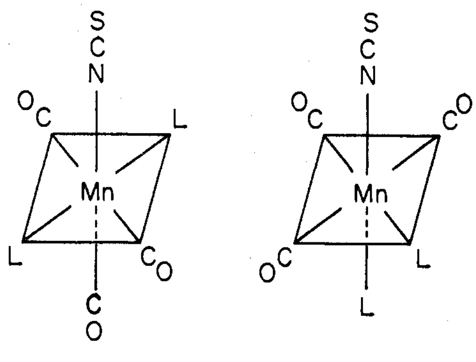
[a] Measured in chloroform solution. [b] Measured in Nujol mull. [c] No CS stretching frequency detectable in the 680–720 cm.$^{-1}$ range; strong ligand absorption at 813 cm.$^{-1}$. [d] No CS stretching frequency detectable in the 780–860 cm.$^{-1}$ range; strong phenyl ring absorption in the 680–720 cm.$^{-1}$ region. For abbreviations, see Tables I and II.

TABLE IV

CN, CO, AND CS STRETCHING FREQUENCIES (CM.$^{-1}$) OF *trans*-[$Mn(CO)_3L_2(NCS)$] COMPLEXES

Complex	CN stretch[a] (SCN)	CO stretches[a]			CS stretch[b] (SCN)
		A_1^2	B_1	A_1^1	
$Mn(CO)_3[P(C_6H_5)_3]_2NCS$	2096 m	2039 w	1957 s	1926 m	820 m
$Mn(CO)_3[As(C_6H_5)_3]_2NCS$	2103 m	2046 w	1963 s	1927 m	814 m
$Mn(CO)_3[Sb(C_6H_5)_3]_2NCS$	2097 m	2033 w	1962 s	1927 m	820 m

[a] Measured in chloroform solution. [b] Measured in Nujol mull. For abbreviations, see Table II.



(a) (b)

Figure 1.—The two possible isomers for *trans*-[$Mn(CO)_3L_2(NCS)$] complexes.

foregoing evidence must not be regarded as unequivocal since some thiocyanato-N compounds are known to absorb considerably above 2100 cm.$^{-1}$ (*vide infra*).

The CN, CO, and CS stretching frequencies of the *cis* tricarbonyls are given in Table III. The presence of three strong carbonyl bands in the spectra supports the structure in which the CO groups are all *cis*. Moreover, most of these complexes exhibit the CS stretching frequency at 800–818 cm.$^{-1}$; this is considered as indicative of their Mn–NCS bonding. The spectrum of $Mn(CO)_3(\gamma\text{-pic})_2NCS$ shows a strong 4-methylpyridine band at 813 cm.$^{-1}$; there is no CS stretching absorption in the 680–720 cm.$^{-1}$ range. Because the CO and CN frequencies of this derivative almost exactly match those of the N-bonded $Mn(CO)_3(py)_2NCS$, it is inferred that the attachment in the former is also through the nitrogen.

The compounds $Mn(CO)_3L_2(SCN)$ (L = $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) exhibit no bands in the 780–860 cm.$^{-1}$ range; strong phenyl ring absorptions preclude detection of the CS stretching bands in the 680–720 cm.$^{-1}$ region. These observations and rather high CN stretching frequencies (2148 cm.$^{-1}$) suggest that the derivatives are S-bonded.

The *trans* tricarbonyls most likely have structures in which the neutral ligands other than CO are *trans*, but each is *cis* to the thiocyanate (Figure 1a). The alternative arrangement—one noncarbonyl neutral ligand *cis* and the other *trans* to NCS (Figure 1b)—cannot be ruled out on the basis of the spectral evidence. Simple group theoretical and symmetry considerations predict that both isomers should exhibit three infrared carbonyl stretching frequencies—one of each weak, strong, and medium intensity. However, in view of the known inertness of the CO *trans* to X in the complexes $Mn(CO)_5X$[17] (X = Cl, Br, I), the latter structure (Figure 1b) is assumed to be less probable. The CN, CO, and CS stretching frequencies, along with their assignments, are listed in Table IV.

All of the CS stretching frequencies occur in the range 814–823 cm.$^{-1}$; this observation leads to a common thiocyanato-N proposed bonding. The data on the CN absorptions support the foregoing assignment; the frequencies (2096–2103 cm.$^{-1}$) are in the region expected for N-bonded thiocyanates.[6,16]

Infrared Spectra of $Mn(CO)_4[As(C_6H_5)_3]SCN$ and $Mn(CO)_4[P(C_6H_5)_3]SCN$ in Acetonitrile.—The final infrared spectra in the 1900–2200 cm.$^{-1}$ range of $Mn(CO)_4[As(C_6H_5)_3]SCN$ in acetonitrile, recorded within 1 min. after dissolution of the carbonyl at 20°, are significantly different from those of the chloroform solutions. Both are shown in Figure 2. The former contains bands at 2141 (w), 2106 (m), 2054 (s), 1961 (s), and 1953 (s) cm.$^{-1}$; in addition, it exhibits a weak-intensity absorption at 814 cm.$^{-1}$, which is missing in the spectra of both the chloroform solutions and Nujol mulls.

The spectra of the arsine complex in $CHCl_3$–CH_3CN

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[17] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

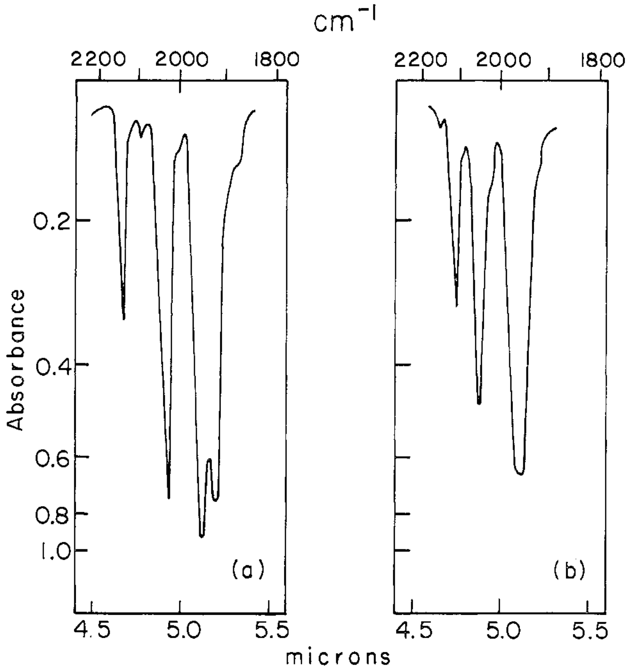

Figure 2.—The infrared spectra in the CN and CO stretching region of $Mn(CO)_4[As(C_6H_5)_3]CNS$ in (a) $CHCl_3$ and (b) CH_3CN.

mixtures show features characteristic of the carbonyl present in each solvent alone. Addition of chloroform or acetonitrile results in rapid changes which indicate an increase in the concentration of the species prevailing in the added solvent. The spectral variations are reversible and easily reproducible. Moreover, thin film spectra show that $Mn(CO)_4[As(C_6H_5)_3]SCN$ is obtained immediately upon evaporation of the solvent from the acetonitrile solutions. There is no detectable decomposition accompanying the above changes.

The carbonyl stretching frequency region spectra of $Mn(CO)_4[P(C_6H_5)_3]SCN$ in acetonitrile, recorded within 1 min. after dissolution of the compound at 20°, are quite complex and resemble those obtained for the arsine derivative in mixed $CHCl_3$–CH_3CN solvents. The spectra are invariant to time; however, as for $Mn(CO)_4[As(C_6H_5)_3]SCN$, they are sensitive to the composition of the solvent. The S-bonded tetracarbonyl may be recovered with little, if any, decomposition upon removal of the acetonitrile.

Discussion

The infrared spectra of the thiocyanatocarbonyl complexes in chloroform solutions and Nujol mulls suggest that (a) all of the tetracarbonyls are S-bonded, (b) the *cis* tricarbonyls containing amines and 1,2-bis(diphenylphosphino)ethane are N-bonded, those with triphenylarsine and -stibine being S-bonded, and (c) the *trans* tricarbonyls are all N-bonded.

Several of these derivatives were prepared both by a direct reaction of $Mn(CO)_5CNS$ with the appropriate ligand and by metathesis involving the corresponding chloro or bromo complex and potassium thiocyanate (Table I). The latter reactions were carried out for several hours at 50–60° and, in all cases, yielded the same linkage isomer as direct replacement of carbon monoxide by the neutral ligand. Thus, it may be concluded that the isolated solids are the thermodynamically more stable thiocyanato isomers. This point is further supported by the nature of the product obtained from the reaction of *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ with 2,2′-bipyridine. Only the complex *cis*-$Mn(CO)_3(bipy)NCS$ was isolated. Hence, replacement of the triphenylstibines by the bidentate 2,2′-bipyridine is accompanied by rearrangement from Mn–SCN to Mn–NCS to yield the thermodynamically stable linkage isomer, which may be also obtained from $Mn(CO)_5CNS$ and the ligand and from *cis*-$Mn(CO)_3(bipy)Br$ and potassium thiocyanate.

It is of interest that the tetracarbonyls prepared in this study are all S-bonded whereas the *cis* and *trans* tricarbonyls, with the notable exceptions of *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$ and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$, are N-bonded in the solid phase and chloroform solutions. To explain these results we suggest, from the evidence on hand, that the extent of $M{=}CO$ π bonding in a thiocyanatocarbonyl complex may play an important role in stabilizing a given mode of metal–thiocyanate attachment. When the π bonding is relatively weak as, for example, in $Mn(CO)_5CNS$,[18] the more polarizable sulfur end is preferred by the metal. The sulfur bonding increases negative charge on the metal and thus enhances $M{=}C{=}O$ π bonding. As the extent of the participation of the metal in π bonding with its carbonyl groups increases, the CO groups make less demand on the metal for negative charge, and the preference of the latter changes from the sulfur to the nitrogen atom. Such situations may arise when the oxidation state of a metal decreases or when carbon monoxide is replaced by ligands of lesser π-bonding capacity. The ion $Cr(CO)_5NCS^-$ affords an example of the former,[19] and the complexes $Mn(CO)_3L_2(NCS)$ and $Fe(CO)_2[P(C_2H_5)_3]_2(NCS)_2$[20] of the latter case. On the other hand, $Mn{=}C{=}O$ π bonding in the tetracarbonyls under investigation is limited by competition of four CO groups for only three metal dπ orbitals. Hence a manganese–sulfur linkage results.

The foregoing point of discussion must not be interpreted as suggestive that the π-bonding capacity of a carbonyl group is to reach its maximum before M—NCS bonding be attained. Instead, it is proposed that the extent of $M{=}C{=}O$ π bonding controls the polarizing ability of the metal and, at some unknown critical stage, changes the preference of the latter of one donor atom of the thiocyanate to the other. Stated in more familiar terms, strong π bonding results in class a, and weak π bonding in class b, metal behavior.[21]

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[18] This statement is arrived at from qualitative considerations. The positive oxidation state of the metal and the presence of more than three CO groups limit the degree of $Mn{=}C{=}O$ π bonding.

[19] A. Wojcicki and M. F. Farona, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964).

[20] G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

[21] For a discussion of class a and b metals, see S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958); also, R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

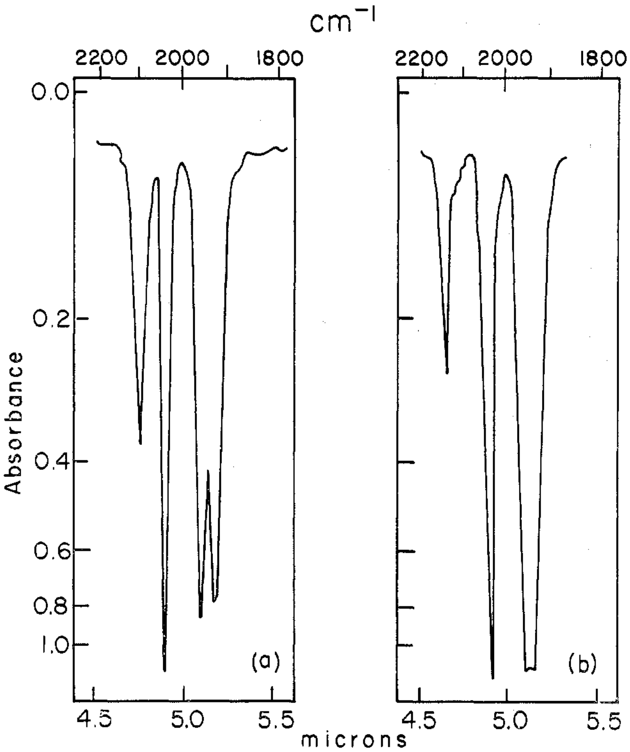


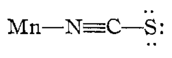
Figure 3.—The infrared spectra in the CN and CO stretching region of (a) *cis*-$Mn(CO)_3(C_5H_5N)_2NCS$ and (b) *cis*-$Mn(CO)_3(p\text{-}H_2NC_6H_4F)_2NCS$, both in $CHCl_3$.

Although the carbonyl stretching regions of the infrared spectra of the derivatives are reasonably straightforward and similar to those of the analogous halogeno complexes, which have been discussed elsewhere,[7,11,14] noteworthy are certain features observed for the N-bonded *cis* tricarbonyls. These compounds may be classified into two groups on the basis of their spectral characteristics. The first group includes the complexes with pyridine, 2,2′-bipyridine, 4-methylpyridine, and 1,2-bis(diphenylphosphino)ethane—ligands that can participate in π bonding; the second group includes the complexes with substituted anilines—ligands that do not π-bond. The representative spectra, those of *cis*-$Mn(CO)_3(py)_2NCS$ and *cis*-$Mn(CO)_3$-(p-fan)$_2$NCS, in the 1900–2200 cm.$^{-1}$ range are shown in Figure 3.

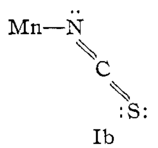
There are two fundamental differences in the spectra of group 1 and 2 complexes. First, the low-frequency bands of group 2 derivatives are closer together than those of group 1.[22] These absorptions may be assigned to the asymmetric stretch of the CO groups *trans* to the amines (or the diphosphine) and to the vibration of the CO *trans* to NCS.[14] It therefore follows that the two bands will be farther apart for the complexes in which the π-bonding capacity of L exceeds that of NCS (group 1) than for those derivatives in which both L and NCS exhibit comparable, and negligible or no π-bonding ability (group 2).

The second and more important point to this discussion is that the CN stretching frequencies of group 2 complexes are significantly higher than those of group 1. Actually, the former fall in the range observed for the S-bonded *cis* tricarbonyls (Table III). We feel that this apparent discrepancy may possibly be rationalized as follows.

One can qualitatively account for the positions of the CN stretching bands by considering structures Ia and Ib.[23] From the infrared spectra it appears that Ia and Ib describe best the bonding in group 2 and 1 *cis* tricarbonyls, respectively. The different Mn–NCS


$Mn{-}N{\equiv}C{-}\ddot{\underset{\cdot\cdot}{S}}{:}$

Ia



Ib

interactions may result from different degrees of competition for manganese π electrons between the carbonyls and other neutral ligands in the two types of complexes. Alone, this would decrease $Mn{=}C{=}O$ π bonding in group 1 relative to that in group 2 derivatives. To compensate for the apparent bond weakening the NCS^- nitrogen electrons in the former group of compounds may be somewhat polarized, thereby increasing negative charge on the manganese and enhancing π bonding between the metal and CO groups. However, the extent of this polarization is still insufficient to effect metal–sulfur linkage for the thiocyanate. In group 2 derivatives, the carbonyls do not compete with the substituted anilines for π bonding with the manganese. Hence less polarization of the NCS^- nitrogen electrons occurs, which corresponds to a greater importance of structure Ia relative to Ib. It is also noteworthy that the p-fluoroaniline and p-toluidine complexes exhibit almost identical spectral features. Thus, the nature of the *para* substituent on the aniline apparently does not significantly affect either the CO or thiocyanate bonding.

If the above variations in the CN stretching frequencies are to be explicable in terms of the two bonding forms (I), then differences in position of the CS stretching absorptions must also be expected for these complexes. Inspection of the spectra in the 780–860 cm.$^{-1}$ range reveals that group 1 derivatives absorb at 813–818 cm.$^{-1}$ whereas those of group 2 absorb at 800–803 cm.$^{-1}$. Qualitatively, the results are as predicted; however, the two ranges of absorption fall close together. Therefore, the foregoing argument must be accepted with some reservation at present.

The two exceptions to N-bonded structures of the thiocyanatotricarbonyls are *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2$-SCN and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$. Here, a possible explanation of the different mode of manganese–thiocyanate attachment may be invoked with the aid of Steward–Briegleb molecular models. These show that considerable steric strain results when two triphenylarsine or -stibine groups are coordinated to the

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(22) The apparent exception is *cis*-$Mn(CO)_3(bipy)NCS$.

(23) Instead of Ib, the bonding form $Mn{=}N{=}C{=}S$ (Ic), in which NCS^- is actually a π donor, may be considered. However, no attempt is made here to differentiate between σ- (Ib) and π-electron (Ic) polarization from the infrared spectra. X-Ray crystallographic data on Mn–NCS angles would be particularly helpful in the evaluation of importance of structural forms Ib and Ic.

metal in *cis* positions. Furthermore, models of the two complexes with linear Mn–NCS moieties demonstrate that the carbon and sulfur atoms of the thiocyanate experience some interaction with the crowded phenyl groups. However, steric hindrance is significantly reduced in models containing angular Mn–S–CN linkages; here, the thiocyanate fits perfectly, with the CN moiety pointing away from the phenyl rings.

It is further of interest that no *cis*-$Mn(CO)_3[P(C_6H_5)_3]_2CNS$ could be prepared in this study. Unsuccessful attempts at the synthesis may be again rationalized with the help of molecular models. In trying to assemble the derivative it was observed that two triphenylphosphine groups cannot be placed in *cis* positions. The difficulty stems from a relatively small size of the phosphorus atom which tends to crowd the phenyl groups by placing them close to the metal. However, with the larger arsenic and antimony atoms the phenyl rings are farther apart, thus reducing the strain. It is pertinent to mention that the attempted synthesis of an analogous complex, *cis*-$Mn(CO)_3[P(C_6H_5)_3]_2Br$, was also unsuccessful,[7] presumably for the same reasons as above.

Although rationalization of the importance of steric hindrance on the basis of molecular models alone must be accepted with reservation, there is experimental evidence in support of the above supposition. Some evidence is provided by the derivative $Mn(CO)_3[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]NCS$, the infrared spectrum of which suggests a nitrogen-bonded structure. Steric hindrance in this molecule is considerably less than in *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$, since only two bulky phenyl groups are bonded to each phosphorus. Thus, there is no longer preferential stabilization of a Mn–SCN linkage, and the N-bonding, found in the other tricarbonyls, also prevails in this chelate. Molecular models of the complex indicate that neither the N- nor unknown S-bonded isomer experiences any significant steric crowding of the phenyl groups.

Additional evidence for steric effects in some of these derivatives may be obtained upon examination of the products afforded by the reactions of $Mn(CO)_5CNS$ with triphenylarsine and -stibine in chloroform at 25°. After 12 hr., the stibine reaction yields almost exclusively (95%) the *cis* tricarbonyl, and the arsine reaction gives a mixture of the *cis* tricarbonyl (60–70%) and tetracarbonyl (30–40%). Recently, Angelici and Basolo[24] observed that the ratio of the rate constants for the dissociation of CO from $Mn(CO)_4[As(C_6H_5)_3]Br$ and $Mn(CO)_4[Sb(C_6H_5)_3]Br$ at 40° is approximately 4:1. Because of structural similarities among the derivatives, it is very likely that the same qualitative order will hold for the analogous thiocyanato complexes. If so, then a better conversion of the tetracarbonyl to the *cis* tricarbonyl with the stibine ligand may be best attributed to steric factors. Since the phenyl groups experience greater steric strain in *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$ than in *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$, the triphenylarsine probably does not compete as effectively as triphenylstibine with the CO for a five-coordinated intermediate, $Mn(CO)_3L(SCN)$, present in solution.

In order to test further the validity of the contention that steric factors are responsible for thiocyanato-S structures of *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$ and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$, the reaction of the N-bonded $Mn(CO)_5NCS$ with triphenylstibine was carried out in acetonitrile. The isolated derivatives were identified by infrared spectroscopy as *trans*-$Mn(CO)_3[Sb(C_6H_5)_3]_2NCS$ (60–80%) and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ (20–40%). No N-bonded *cis* tricarbonyl could be detected in the products. Since the reaction conditions were ideally adapted to promote formation of such isothiocyanato complex—no rearrangement from Mn–SCN to Mn–NCS is necessary—the evidence supports S-bonding in the two *cis* tricarbonyls on steric grounds.

The statement that no thiocyanate–manganese linkage rearrangement need occur in the formation of the unknown N-bonded *cis* tricarbonyl is based on the premise that the precursor of the complex is the isothiocyanate, $Mn(CO)_4[Sb(C_6H_5)_3]NCS$, rather than its S-bonded isomer, known to exist in the solid state and chloroform solutions. In order to shed some light on the nature of the tetracarbonyl complexes in acetonitrile, which, as already reported,[3] promotes N-bonding in $Mn(CO)_5CNS$, the spectrum of $Mn(CO)_4[As(C_6H_5)_3]SCN$ in CH_3CN was recorded and compared with that of the chloroform solutions. The two spectra are significantly different (Figure 2). The former exhibits a weak intensity band at 814 cm.$^{-1}$, which is assigned to the CS stretching mode of an N-bonded thiocyanate. Consistent with the appearance of this peak, missing in the chloroform solution spectra, the CN stretching frequency shifts to a lower value—from 2149 cm.$^{-1}$ in $CHCl_3$ to 2106 cm.$^{-1}$ in CH_3CN. The strong bands at 2054, 1961, and 1953 cm.$^{-1}$ are assigned to the carbonyl stretching modes; the weak absorption at 2141 cm.$^{-1}$ possibly may indicate a small amount of the S-bonded isomer.

The most plausible explanation of these spectral changes involves linkage isomerization from Mn–SCN to Mn–NCS. This is supported by both the appearance of the CS stretching frequency in the 780–860 cm.$^{-1}$ range and shift of the CN stretching absorption to lower wave numbers.[6,16] Another possibility, *i.e.*, dissociation of the triphenylarsine to form either a trigonal-bipyramidal (C_{3v} or C_{2v}) or square-pyramidal (C_s) $Mn(CO)_4NCS$ or, alternatively, *cis*-$Mn(CO)_4(CH_3CN)(NCS)$, cannot be ruled out on spectral grounds.[25] However, in view of the observed reactivity of $Mn(CO)_5NCS$ toward $Sb(C_6H_5)_3$ in acetonitrile to form the tricarbonyls, and because the spectrum suggests that only one predominant carbonyl species is present, such complete elimination of the arsine from

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(24) R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).

(25) For a discussion of carbonyl stretching frequencies of the infrared spectra of $M(CO)_4L$ complexes, see F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

the complex must be considered less likely than linkage rearrangement.

Solutions of the monotriphenylphosphine derivative in acetonitrile also exhibit infrared spectra distinct from those recorded for the chloroform solutions. However, the reaction that goes to a virtual completion with the arsine complex now appears to be arrested at an intermediate stage. Preliminary spectral measurements indicate attainment of an equilibrium, possibly between the S- and N-bonded linkage isomers of the tetracarbonyl. However, a more complicated behavior, involving also partial replacement of triphenylphosphine by acetonitrile, cannot be ruled out at present.

Finally, it is of interest to compare and contrast our results with those obtained by Burmeister and Basolo[6] for some palladium(II) square-planar thiocyanato complexes.[26] The latter study demonstrated that small differences in ligand structure frequently cause changes in metal–thiocyanate attachment. For example, the complex $Pd(py)_2(NCS)_2$[27] is N-bonded whereas the 4-methylpyridine analog is S-bonded. Furthermore, $Pd[P(C_6H_5)_3]_2(NCS)_2$ and the thermodynamically stable isomer of $Pd[As(C_6H_5)_3]_2(CNS)_2$ are isothiocyanates, but $Pd[Sb(C_6H_5)_3]_2(SCN)_2$ is a thiocyanate. These variations in bonding were attributed to steric and/or electronic factors. By way of contrast, the six-coordinate manganese(I) complexes reported herein do not exhibit such striking differences in metal–thiocyanate bonding with small changes in ligand structure. The derivatives $Mn(CO)_3(py)_2NCS$ and $Mn(CO)_3(\gamma\text{-pic})_2NCS$ contain the same type of Mn–CNS linkage, as do also all carbonyls of the same stereochemistry containing $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$. Therefore, comparison of the results of the two investigations furnishes additional support to our contention that the degree of π bonding, rather than small electronic and steric differences among other coordinated ligands, is the most important single factor determining the type of metal–thiocyanate bonding in carbonyl complexes. Whether this explanation is general or limited only to six-coordinate systems cannot be ascertained at present. However, studies are in progress on thiocyanatocarbonyl complexes of other geometries in order to resolve the issue in question.

Acknowledgment.—The financial support of this investigation by the National Science Foundation is gratefully acknowledged.

[26] Palladium(II) rather than platinum(II) is selected because of the smaller size of the former, which makes comparison with manganese(I) more meaningful.

[27] This and the other thiocyanato complexes of Pd(II) most likely have *trans* structures; see ref. 6.

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Chloro Complexes of Copper(II) and Copper(I) in Acetonitrile

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The stepwise formation constants of the chloro complexes of copper(II) and of copper(I) in acetonitrile have been evaluated by a combination of spectrophotometric and electrochemical methods. Log K values in acetonitrile for the copper(II) complexes are 9.7, 7.9, 7.1, and 3.7, and for the copper(I) complexes 4.9 and 5.9.

The stepwise formation constants of $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$ in water are only 1, 0.2, 0.04, and 0.01, respectively.[1] Because copper(II) and chloride ions are significantly more weakly solvated in acetonitrile than in water,[2] information on the chloro complexes of copper(II) in acetonitrile is, therefore, of considerable fundamental importance. The much higher solvation energy of copper(I) ion in acetonitrile than in water makes the study of the chloro complexes of copper(I) also of special interest.

From spectrophotometric study of acetonitrile solutions of copper(II) and chloride, Baaz, Gutman, Hampel, and Masagner[3] have estimated the stepwise formation constants of the chloro complexes of copper(II) to be $K_{CuCl^+} > K_{CuCl_2} \geq K_{CuCl_3^-} > K_{CuCl_4^{2-}}$. Bromide ion and copper(II) ion have been found to form only two species, $CuBr_3^-$ and $CuBr_4^{2-}$, in acetonitrile.[4] Quantitative study of these complexes in acetonitrile is complicated by the oxidation of bromide by copper(II).

Experimental

Reagent grade acetonitrile was distilled twice from phosphorus pentoxide and the fraction boiling at 81.0 ± 0.5° collected. Tetraethylammonium perchlorate, $(C_2H_5)_4NClO_4$, was prepared by adding a slight excess of 70% reagent grade perchloric acid to Eastman aqueous 10% tetraethylammonium hydroxide. The product was recrystallized twice from water and dried under vacuum at 80° for 48 hr. Eastman tetraethylammonium chloride, $(C_2H_5)_4NCl$, was purified by recrystallization from acetonitrile. Copper(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) was dried *in vacuo* at 70° for 48 hr.

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[1] J. Bjerrum, *Kem. Maanedsblad*, **26**, 24 (1945).

[2] I. M. Kolthoff and J. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).

[3] M. Baaz, V. Gutman, G. Hampel, and J. Masagner, *Monatsh. Chem.*, **93**, 1416 (1962).

[4] J. Barnes and D. Hume, *Inorg. Chem.*, **2**, 444 (1963).