metric apparatus[5] at 0° filled with methylene chloride saturated carbon monoxide was placed a solution of 0.41 g. of diiodocarbonylcyclopentadienylcobalt in 10 ml. of methylene chloride, and 1.0 ml. of 1.0 *M* dipyridyl in methylene chloride was added. The reaction was complete in less than 1 min. A brown precipitate was formed and 25 ml. of gas (0.8 mmole) was evolved. The insoluble product was separated by centrifuging and then recrystallized by dissolving it in about 40 ml. of warm methanol and adding ether. Short black needles of the product crystallized from the solution. There was obtained 0.30 g. of product.

Bromodipyridylcyclopentadienylcobalt Bromide.—To the crude dibromocarbonylcyclopentadienylcobalt prepared from 2 mmoles of dicarbonylcyclopentadienylcobalt as described above (not recrystallized) was added 50 ml. of methylene chloride. The solution at room temperature was centrifuged to remove a small amount of insoluble material, and then 2.0 ml. of 1.0 *M* dipyridyl in methylene chloride was added. A purple solid soon crystallized from the solution. The product was separated by centrifuging and recrystallized three times from methanol by adding ether. About 0.1 g. of purple needles was obtained.

Chlorodipyridylcyclopentadienylcobalt Hexafluorophosphate.—A sample of dichlorocarbonylcyclopentadienylcobalt was prepared exactly as described above and to the reaction mixture, cooled in a Dry Ice–acetone mixture, was added 2.0 ml. of 1.0 *M* dipyridyl in methylene chloride. The cold solution was centrifuged, and the purple solid obtained was dried under vacuum. The crude product was recrystallized from methanol by adding an equal volume of ether. The crystalline product was then dissolved in 25 ml. of methanol, and a solution of 0.5 g. of ammonium hexafluorophosphate in 5 ml. of methanol was added. The purple precipitate was filtered off and air dried. About 0.1 g. of the hexafluorophosphate was obtained.

CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

The Synthesis of Thiocyanatopentacarbonylmanganese(I) and Studies on Manganese–Thiocyanate Bonding[1]

BY MICHAEL F. FARONA[2] AND ANDREW WOJCICKI

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The synthesis of thiocyanatopentacarbonylmanganese(I) by the reaction of sodium pentacarbonylmanganate(−I) and thiocyanogen chloride is reported. Infrared spectral and, where appropriate, electrical conductance studies suggest that the complex is S-bonded in the solid state, almost completely N-bonded in acetonitrile, and that equilibrium between the two linkage isomers prevails in dichloromethane, 1,2-dichloroethane, chloroform, and ethyl acetate. A possible explanation for the different modes of metal–thiocyanate attachment in the isoelectronic $Mn(CO)_5SCN$ (solid state) and $Cr(CO)_5NCS^-$ ion is presented. Attempted preparations of dithiocyanatotetracarbonyliron(II) have been unsuccessful.

Introduction

Thiocyanato complexes of the transition elements have received considerable attention during recent years.[3–11] The ambidentate nature of the ligand has stimulated a number of investigations primarily directed at the elucidation of various factors which influence the two modes (M–SCN and M–NCS) of metal–thiocyanate attachment[3–7] and at the development of physicochemical techniques for the diagnosis of the type of binding.[5–11]

The reported studies did establish that both steric[3,4] and electronic[4–7] factors affect the nature of M–CNS bonding in complexes containing metals in intermediate and high oxidation states. Nevertheless, a complete explanation of the metal's preference for the sulfur end of the ligand in some compounds, and for the nitrogen end in others, is still lacking at present. Furthermore, neglected in all investigations have been complexes of low-valent metals. Although the literature does contain isolated reports of the synthesis of few compounds, for example, $Fe(CO)_2(P(C_2H_5)_3)_2(NCS)_2$[12,13] and $Rh(CO)L_2CNS$[14] ($L = P(C_6H_5)_3, As(C_6H_5)_3, Sb(C_6H_5)_3$), these were not prepared for a study of the bonding.

In order to fill this void we have commenced an investigation of thiocyanato derivatives of the metal carbonyls. Such compounds are expected to possess many properties in common with the carbonyl halides[15] and hence may provide systems ideally suited to a systematic study of various factors that influence one mode of metal–thiocyanate attachment in preference to the other. Structurally, the complexes should exhibit several different geometries, which would render possi-

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

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(13) Henceforth NCS designates N-bonding and SCN S-bonding; CNS denotes that either the bonding is not known or both isomers are present in equilibrium.

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ble a thorough investigation of stereochemical effects on the bonding. Electronic features could also be explored on isostructural species, for example, the thiocyanato analogs of $Mn(CO)_5I$, $Cr(CO)_5I$, and $Cr(CO)_5I^-$.

Manganese carbonyl was selected for the initial investigation because of the relatively high stabilities of the derivatives $Mn(CO)_5X$[15] (X = unidentate anionic ligand) and their C_{4v} (or approximately C_{4v}) molecular symmetry, which facilitates structural assignments on the basis of infrared spectroscopy. This paper reports the synthesis of the first simple thiocyanato metal carbonyl, $Mn(CO)_5SCN$,[16] and describes some studies on the nature of its Mn–CNS attachment in both the solid state and solutions. Communicated later will be an investigation on the derivatives of this parent thiocyanatocarbonyl.

Experimental

Materials.—Dimanganese decacarbonyl was purchased from the Ethyl Corporation; additional samples were kindly provided by Professor H. B. Gray of Columbia University and Dr. J. A. Ibers of the Brookhaven National Laboratory. The compound was purified by sublimation [50° (0.01 mm.)]. Iron pentacarbonyl was obtained from Antara Chemicals and used without further purification. The carbonyls $Mn(CO)_5Cl$,[17] $HgFe(CO)_4$,[18] and $Fe_3(CO)_{12}$[19] were prepared as described in the literature.

Solutions of thiocyanogen in hexane were prepared by the oxidation of suspended lead thiocyanate with pure bromine[20] under scrupulously dry conditions. Solutions of thiocyanogen chloride in hexane were prepared as described in the literature.[21] Both were filtered and used immediately for subsequent reactions.

Solvents of analytical reagent grade (*n*-hexane, dichloromethane, 1,2-dibromoethane, chloroform, 1,2-dichloroethane, ethyl acetate, acetone, and methanol) were degassed before use. Other solvents were purified as follows. Tetrahydrofuran was fractionally distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. The fraction boiling at 66° was collected. Nitromethane was purified as described in the literature.[22] Acetonitrile was first refluxed over and distilled from calcium hydride, then from phosphoric oxide, and again from calcium hydride. In each distillation, only the fraction boiling at 81–82° was collected. Pure nitrobenzene[23] was obtained from Mr. J. Walther of The Ohio State University Chemistry Department. Low boiling (30–60°) petroleum ether was used without further purification.

Preparation of $Mn(CO)_5SCN$.—All operations were carried out in a dry, nitrogen-atmosphere box. In a typical preparation, sodium pentacarbonylmanganate(–I), from 3.0 g. (0.0077 mole) of dimanganese decacarbonyl and sodium amalgam (0.45 g. of sodium and 54 g. of mercury) in 50 ml. of freshly distilled tetrahydrofuran, was added dropwise through a filter, with stirring, to a solution of thiocyanogen chloride, from 0.54 g. (0.0077 mole) of chlorine and a slight excess of thiocyanogen (0.0085 mole) in 40 ml. of hexane. Addition of the carbonylate gradually changed the color of the thiocyanogen chloride solution from bright yellow to yellow-orange, and formation of a white precipitate, later shown to be sodium chloride, was observed. On completion of the addition, the reaction mixture was removed from the drybox, and the solvent was evaporated [25° (~20 mm.)]. The residue was extracted with 25 ml. of chloroform, the mixture was filtered, and the volume of the orange solution was reduced to about 5 ml. in a stream of nitrogen. Slow addition, with stirring, of 200 ml. of low boiling petroleum ether afforded a golden-yellow precipitate, which was washed several times with petroleum ether and dried [25° (0.01 mm.)] for 30 min. The yield was 2.73 g. (70%). The compound may be purified by recrystallization from a chloroform–petroleum ether mixture.

Anal. Calcd. for $Mn(CO)_5SCN$: C, 28.47; N, 5.53; S, 12.67; Mn, 21.70; O, 31.60; Cl, 0.0; mol. wt., 253. Found: C, 28.04; N, 5.50; S, 12.55; Mn, 21.60; O, 31.55, 31.53, 31.30; Cl, 0.0; mol. wt., 247, 259 (cryoscopic in nitrobenzene, *ca.* 10^{-2} *M* solution).

The compound decomposes on heating at 156°. It is diamagnetic and a nonelectrolyte in nitromethane (molar conductivity of a 10^{-3} *M* solution = 0.7 ohm^{-1} $cm.^2$). The complex is readily soluble in dichloromethane, ethyl acetate, acetone, acetonitrile, and methanol, sparingly soluble in chlorobenzene and ether, and insoluble in cyclohexane, carbon disulfide, carbon tetrachloride, and water. It is stable in the absence of light and under nitrogen.

Reaction of $Mn(CO)_5CNS$ with Pyridine.—The thiocyanatocarbonyl complex (0.0628 g., 0.248 mmole) and pyridine (0.2 ml., 2.4 mmoles) in 8 and 4 ml. of 1,2-dibromoethane, respectively, were placed, separately, in two mixing compartments of a Y-shaped flask connected to a gas buret. After equilibrium had been attained, the contents of the flask were mixed and allowed to stand for 6 hr. to ensure completion of the reaction. The volume of carbon monoxide collected at 28° and 736 mm., corrected for the vapor pressure of the solvent, was 12.8 ml. (0.504 mmole). Removal of the solvent and excess pyridine [28° (~20 mm.)] afforded *ca.* 100% yield of $Mn(CO)_3(C_5H_5N)_2NCS$, which was identified by comparison of its infrared spectrum with that of a previously prepared and characterized sample.[16]

Attempted Preparations of $Mn(CO)_5CNS$. (a) **Reaction of $Mn_2(CO)_{10}$ with $(SCN)_2$.**—Equimolar amounts (*ca.* 3 mmoles) of dimanganese decacarbonyl and thiocyanogen of various concentrations in tetrahydrofuran were stirred for 1 hr. at 25°. No reaction occurred. At 45°, a red precipitate, presumably polymeric thiocyanogen (infrared spectrum), was obtained. The infrared spectrum of the solution showed that dimanganese decacarbonyl remained unreacted.

(b) **Reaction of $NaMn(CO)_5$ with $(SCN)_2$.**—Sodium pentacarbonylmanganate(–I) in tetrahydrofuran was added dropwise, with stirring under nitrogen, to an equimolar (*ca.* 0.01 mole) amount of thiocyanogen in hexane. The mixture was then treated as described for the reaction of the carbonylate salt with thiocyanogen chloride. In some experiments the product was the thiocyanatopentacarbonyl complex; in others, only dimanganese decacarbonyl was isolated (infrared spectral characterization). Addition of thiocyanogen to the carbonylate salt invariably yielded dimanganese decacarbonyl.

(c) **Reaction of $Mn(CO)_5Cl$ with KSCN.**—Chloropentacarbonylmanganese(I) (*ca.* 0.01 mole) and potassium thiocyanate (*ca.* 0.1 mole) in methanol were heated under nitrogen for 2 hr. at 50°. The solvent was evaporated [25° (~20 mm.)], and the infrared spectrum of the residue showed that no thiocyanatopentacarbonyl complex was present.[24]

Attempted Preparations of $Fe(CO)_4(CNS)_2$. (a) **Reaction of $Fe(CO)_5$ with $(SCN)_2$.**—A solution of thiocyanogen (2–9 mmoles) in petroleum ether was added dropwise to an equimolar amount of iron pentacarbonyl in the same solvent at 25° until a vigorous evolution of gas ceased. The resultant brown precipitate did not contain carbonyl groups (infrared spectrum).

When the same reactants were mixed at –20°, a brown precipitate formed without evolution of carbon monoxide. The solid was stable up to 2°, at which temperature it began to lose CO. Attempts to obtain a reproducible infrared spectrum of this compound were unsuccessful.

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TABLE I

CN, CO, AND CS STRETCHING FREQUENCIES (CM.$^{-1}$) OF $Mn(CO)_5CNS$ IN VARIOUS MEDIA[a]

Solvent	CN and CO stretch							CS stretch
Nujol mull	2160 sh,	2138 m,	2084 w,	2043 s, br,	1958 s, br			676 w
Acetonitrile	2141 w,	2113 m,	2053 s,	1958 ms				813 m
Dichloromethane	2156 m,	2140 m,	2110 vw,	2096 w,	2058 s,	2036 s,	1950 ms, br	...[b]
1,2-Dichloroethane	2162 m,	2139 m,	2110 vw,	2094 w,	2060 s,	2031 s,	1960 ms, br	810 w
Chloroform[c]	2162 m,	2144 m,	2110 vw,	2099 w,	2060 s,	2037 s,	1957 ms, br	...[b]
Ethyl acetate	2159 m,	2138 m,	2107 vw,	2096 w,	2058 s,	2034 s,	1950 ms, br	801 w

[a] Recorded at 20°. [b] No band discernible; solvent absorptions. [c] Previously reported spectrum (ref. 16) was measured under very low resolution. Abbreviations: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

(b) **Reaction of $HgFe(CO)_4$ with $(SCN)_2$.**—Thiocyanogen (2 mmoles) in petroleum ether was added dropwise to a suspension of $HgFe(CO)_4$ (1 mmole) in petroleum ether at 0–25°. Gas evolution was observed and the yellow color of the suspension gradually changed to brown. The infrared spectrum of the brown solid revealed no carbonyl bands.

(c) **Reaction of $Fe_3(CO)_{12}$ with $(SCN)_2$.**—Thiocyanogen (3 mmoles) dissolved in petroleum ether was added dropwise to a suspension of $Fe_3(CO)_{12}$ (1 mmole) in the same solvent. No reaction occurred at 25°. At 50°, gas evolution was observed; however, the product was shown not to contain bands in the metal carbonyl stretching frequency region.

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. To record solution spectra at temperatures higher than that of the room, the cell was placed in a small oven constructed from a piece of copper *ca.* 7 cm. wide and bent to fit exactly around the cell and holder. The oven was heated by means of a nichrome wire, and the temperature of the solution was measured with an accuracy of ±2°. Solids were examined in the form of Nujol mulls or thin films. In the latter technique, a drop of solution was placed on a NaCl plate and the solvent was allowed to evaporate. The process was repeated until a solid film of the desired thickness was obtained.

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

Magnetic Susceptibility.—Measurements on acetone solutions were made at room temperature by the Gouy method. A correction for the diamagnetism of the tube and solvent was applied.

Analyses.—For manganese content the compound was heated with nitric acid to oxidize the metal to manganese(II). Manganese was then further oxidized with potassium periodate and determined spectrophotometrically as permanganate.[25] Other elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., and by A. Bernhardt Microanalytical Laboratories of the Max Planck Institute, Mulheim, Germany.

Results

Preparation and Properties of $Mn(CO)_5SCN$.—An attempted preparation of thiocyanatopentacarbonylmanganese(I) by the reaction of $Mn_2(CO)_{10}$ and $(SCN)_2$ at 45° resulted in the formation of only a thiocyanogen polymer. Another synthetic method tried—addition of $NaMn(CO)_5$ to a thiocyanogen solution—afforded, but with poor reproducibility, the complex $Mn(CO)_5SCN$. The latter is most conveniently prepared by a slow addition of $NaMn(CO)_5$ in tetrahydrofuran to thiocyanogen chloride in hexane.

The monomeric pentacarbonyl formulation of the thiocyanato complex is supported by a complete chemical analysis, including that of oxygen, and by the molecular weight determination in nitrobenzene. Additional evidence for the monomeric ($Mn(CO)_5CNS$) rather than dimeric ($Mn_2(CO)_8(CNS)_2$) nature of the product was obtained from the measurement of the volume of CO evolved in the quantitative reaction of the carbonyl with pyridine (eq. 1). From the reaction of 0.0628 g. (0.248 mmole based on the monomer, 0.140 mmole based on the dimer) of the thiocyanatocarbonyl with an excess amount of pyridine, 0.504 mmole of CO was evolved. For the monomeric pentacarbonyl complex, evolution of 0.496 mmole of CO is expected, whereas for the tetracarbonyl dimer, displacement of 0.279 mmole of CO is predicted from eq. 2.

$$Mn(CO)_5CNS + 2C_5H_5N \longrightarrow Mn(CO)_3(C_5H_5N)_2NCS + 2CO \quad (1)$$

$$Mn_2(CO)_8(CNS)_2 + 4C_5H_5N \longrightarrow 2Mn(CO)_3(C_5H_5N)_2NCS + + 2CO \quad (2)$$

The thiocyanatocarbonyl complex resembles the known halogenopentacarbonyls of manganese in being diamagnetic and soluble in more polar organic solvents. However, unlike the latter, it does not sublime *in vacuo* up to 110°; it decomposes in a capillary at 156°.

Infrared Spectrum of Solid $Mn(CO)_5SCN$.—The infrared CN, CO, and CS stretching frequencies of the complex in a Nujol mull are listed in Table I. Two features merit special comments. First, the spectrum shows an absorption band at 676 cm.$^{-1}$, which on the basis of the reported studies by both Turco and Pecile[7] and Lewis, *et al.*,[6] is assigned to the CS stretching mode. Since the known S- and N-bonded thiocyanato complexes absorb in the ranges 690–720 and 780–860 cm.$^{-1}$,[7] respectively, the spectral evidence supports an Mn–SCN attachment in the solid $Mn(CO)_5SCN$.

Secondly, the spectrum in the 1900–2200 cm.$^{-1}$ region consists of five bands, the highest frequency one (2160 cm.$^{-1}$) being most probably due to the CN stretching mode.[26] The remaining absorptions (CO stretches) may be best assigned on the basis of relative positions and intensities as follows[27]: 2138 cm.$^{-1}$, A_1^2; 2084

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(25) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1950, p. 430.

(26) The assignment is not unequivocal; it is possible that both the 2160 and 2138 cm.$^{-1}$ bands result from a CN stretch, the splitting being due to crystal lattice disorder. If so, then the A_1^2 carbonyl absorption may be masked by the 2138 cm.$^{-1}$ band.

(27) See L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962); also F. A. Cotton, *ibid.*, **3**, 702 (1964), and previous papers with C. S. Kraihanzel. Although solid phase infrared spectra of metal carbonyls must be interpreted with caution, the spectrum of $Mn(CO)_5SCN$ appears to be rather straightforward and the following band assignment is made with reasonable confidence. It constitutes a useful basis for subsequent discussion, provided that no quantitative significance is attached to the listed wave numbers.

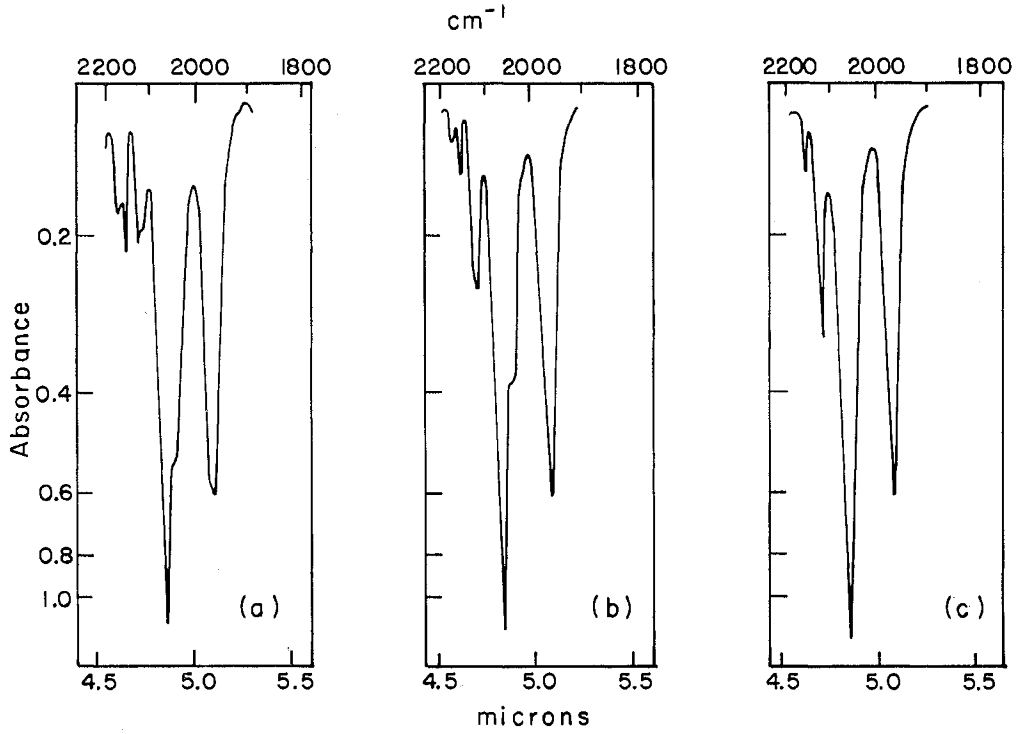

Figure 1.—Infrared spectra of $Mn(CO)_5CNS$ in the CN and CO stretching region; ~9 mg./ml. in CH_3CN, 0.1-mm. cell thickness, at 20°: (a) immediately upon dissolution; (b) after ~3 min.; (c) final, after ~20 min.

cm.$^{-1}$, B_1; 2043 cm.$^{-1}$; E; and 1958 cm.$^{-1}$, $A_1{}^1$. Since M–S–CN angles in the known thiocyanato-S compounds are *ca.* 120°,[6] the molecular symmetry of $Mn(CO)_5SCN$ is expected not to be higher than C_s. Hence the B_1 mode, which is infrared inactive for rigorous C_{4v} symmetry, gains a little intensity in the spectrum.

Infrared Spectrum and Conductivity of $Mn(CO)_5NCS$ in Acetonitrile.—Infrared spectral measurements in the 1900–2200 cm.$^{-1}$ region on a freshly prepared solution of $Mn(CO)_5SCN$ in acetonitrile reveal that a very striking change in the absorption band pattern takes place on standing (Figure 1). Accompanying this change is the appearance of a medium-intensity band at 813 cm.$^{-1}$. The final spectrum, which is obtained after *ca.* 20 min. at 20°, suggests rigid C_{4v} molecular symmetry of the complex. The CN, CO, and CS stretching frequencies are listed in Table I.

Examination of relative intensities and positions of the bands leads to the following assignment: 2141 cm.$^{-1}$, $A_1{}^2$ (CO); 2113 cm.$^{-1}$, ν_3 SCN (C–N stretch); 2053 cm.$^{-1}$, E (CO); 1958 cm.$^{-1}$, $A_1{}^1$ (CO); and 813 cm.$^{-1}$, ν_1 SCN (C–S stretch). The band at 813 cm.$^{-1}$, which is absent in the spectrum of both the solvent and $Mn(CO)_5X$ (X = Cl, Br, I) complexes, points to a rearrangement from the $Mn(CO)_5SCN$ to the $Mn(CO)_5NCS$ isomer. In support of the N-bonded structure of the thiocyanatocarbonyl in solution is also a shift of the CN absorption band to lower frequencies[5]—from 2160 cm.$^{-1}$ in the solid state to 2113 cm.$^{-1}$ in acetonitrile. Moreover, the B_1 carbonyl stretching mode, detectable for $Mn(CO)_5SCN$ in Nujol, is, as expected,[28] infrared inactive for the complex in this solvent.

Electrical conductivities of acetonitrile solutions of the thiocyanatocarbonyl increase slowly with time. Freshly prepared solutions (10^{-3} *M*) exhibit molar conductivities of <7 ohm^{-1} cm.^{2} at 25°; this value increases to 8.6 ohm^{-1} cm.^{2} at the time of virtually complete conversion to the N-bonded isomer. An additional increase of about 6 ohm^{-1} cm.^{2} takes place over a period of 1 hr. and may be due to either a slow decomposition or ionization of the complex. A similar behavior was observed for acetonitrile solutions of $Mn(CO)_5Cl$ ($10^{-3}M$), which exhibit the initial molar conductivity of 6.0 ohm^{-1} cm.^{2} at 25°.[29] Since under the same conditions the molar conductivity of $(C_6H_5)_4AsCl$, a uni-univalent electrolyte, is 138 ohm^{-1} cm.^{2}, the thiocyanatocarbonyl complex is not more than about 7% ionized, perhaps into $Mn(CO)_5(CH_3CN)^+$ and NCS^-. That the concentration of a cationic species is indeed low receives further support from the infrared spectrum of $Mn(CO)_5NCS$ (*vide supra*), which is consistent with the existence of only one major carbonyl complex in solution.

An attempt was made to isolate the N-bonded isomer by allowing the acetonitrile to evaporate slowly from the solution placed on an infrared sodium chloride plate. When solvent bands are no longer discernible (*ca.* 5 min. at 25°), the thin film spectrum matches that recorded for the S-bonded complex in Nujol. The recovery of $Mn(CO)_5SCN$ is virtually quantitative.

Infrared Spectra of $Mn(CO)_5CNS$ in Other Solvents.

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[28] The linear Mn–N–CS arrangement results in rigid C_{4v} molecular symmetry of $Mn(CO)_5NCS$. See ref. 6 for X-ray data on thiocyanato-N complexes.

[29] For further examples of such behavior see C. C. Addison, M. Kilner, and A. Wojcicki, *J. Chem. Soc.*, 4839 (1961).

—By way of contrast, the spectra of $Mn(CO)_5CNS$ in dichloromethane, 1,2-dichloroethane, chloroform, and ethyl acetate are all similar (Table I), but considerably more complex than those in Nujol and acetonitrile. The 1,2-dichloroethane solution spectrum in the CN and CO stretching frequency region at 20° is given in Figure 2.

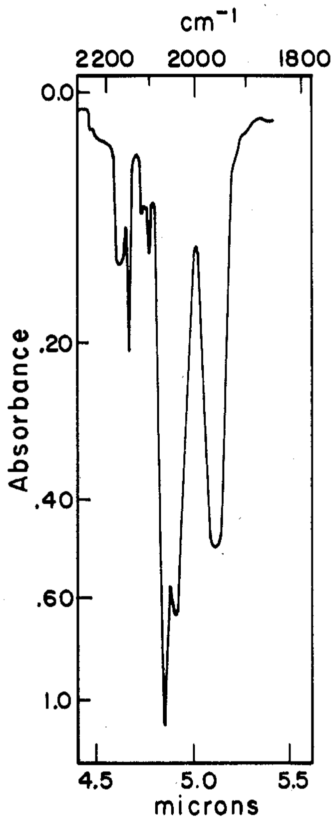

Figure 2.—The infrared spectrum of $Mn(CO)_5CNS$ in the CN and CO stretching region; ~10 mg./ml. in CH_2ClCH_2Cl, 0.1-mm. cell thickness, at 20°.

The spectra of 1,2-dichloroethane and ethyl acetate solutions exhibit weak-intensity bands at 810 and 801 cm.$^{-1}$, respectively; these are assigned to the CS stretching mode of the N-bonded isomer, $Mn(CO)_5NCS$. The bands gain intensity and undergo a small shift (<10 cm.$^{-1}$) to higher frequencies in mixed 1,2-dichloroethane– and ethyl acetate–acetonitrile solvents. Similar absorptions are not discernible in dichloromethane and chloroform solutions, perhaps because of intense solvent bands.

Addition of acetonitrile to dichloromethane, 1,2-dichloroethane, chloroform, or ethyl acetate solutions of $Mn(CO)_5CNS$ significantly alters the relative intensity patterns of the CO and CN stretching bands. All of the spectra in mixed solvents are dependent on the composition of the latter and can be readily reproduced. Moreover, the reversibility of these changes precludes decomposition of the complex.

A similar behavior is also observed when the spectra are recorded at different temperatures (17–40°). Qualitatively, for 1,2-dichloroethane solutions, the bands at 2162, 2139, 2094, 2060, and 1960 cm.$^{-1}$ lose some intensity whereas those at 2110 and 2031 cm.$^{-1}$ gain intensity with increasing temperature. In addition, a new absorption, first detectable as a shoulder on the 1960 cm.$^{-1}$ peak, eventually appears at 1973 cm.$^{-1}$. Again, variations in the relative band intensities are reversible for all solutions, and the complex $Mn(CO)_5SCN$ may be recovered with little, if any, decomposition upon removal of the solvent.

The above spectral changes are consistent with the existence of an equilibrium between the S- and N-bonded linkage isomers. A quantitative study of these systems is now in progress.

Attempted Preparations of $Fe(CO)_4(CNS)_2$.—The reactions of thiocyanogen with $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $HgFe(CO)_4$ at 25–50° afforded brown, noncarbonyl solids, which were not further characterized. At −20°, iron pentacarbonyl reacts with thiocyanogen to produce an unstable carbonyl complex.[30] This compound loses all of its carbon monoxide at 2°; no evidence could be obtained for an intermediate $Fe(CO)_4(CNS)_2$ during decomposition.

Discussion

These studies suggest that thiocyanatopentacarbonylmanganese(I) is S-bonded in the solid state, almost completely N-bonded in acetonitrile, and that equilibrium between the two linkage isomers prevails in dichloromethane, 1,2-dichloroethane, chloroform, and ethyl acetate.

The infrared spectrum of the S-bonded isomer in Nujol reveals a very interesting feature, *i.e.*, an unusually low frequency of the A_1^1 carbonyl stretching mode. The band at 1958 cm.$^{-1}$ is to be compared with the A_1^1 fundamental absorptions at 1999, 2001, and 2003 cm.$^{-1}$ reported for manganese pentacarbonyl chloride, bromide, and iodide, respectively, in carbon tetrachloride solutions.[31] The frequency of the E mode is only slightly lower for $Mn(CO)_5SCN$ than for the halogenopentacarbonylmanganese(I) complexes.

The low frequency of the A_1^1 carbonyl fundamental in $Mn(CO)_5SCN$ is indicative of a significant amount of π-bonding between the metal and the CO *trans* to the thiocyanate (henceforth CO(1)). Such a pronounced $Mn \rightarrow CO(1)$ π-interaction most likely results from a strong electron-donor property of sulfur and from the latter's inability to compete effectively with the CO groups for the manganese π-electrons. Polarization of the sulfur electrons by the metal increases negative charge on the manganese; this in turn promotes $Mn \rightarrow CO$ π-bonding. Because of the symmetry of the metal $d\pi$-orbitals, the CO *trans* to thiocyanate will benefit most from sulfur's inability to effectively π-bond in the system. The result will be a strong $Mn{=}CO(1)$ bond and hence the observed low CO(1) stretching frequency.

It is of interest that the isoelectronic ion, $Cr(CO)_5$

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[30] It is of interest that the reaction of iron pentacarbonyl and iodine at low temperatures produces $Fe(CO)_5I_2$, a compound of unknown structure. See W. Hieber and G. Bader, *Ber.*, **61B**, 1717 (1928).

[31] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

NCS^-, contains an N-bonded thiocyanate and exhibits no tendency to rearrange to the S-bonded isomer in either the solid state or solutions.[32] Since all of the other factors are kept constant, the difference in the bonding in the chromium(0) and manganese(I) species must be attributed to the charge on the metal. Thus, the driving force for the stabilization of the S-bonded isomer of a more positive manganese(I) may be the latter's preference for the polarizable end of the thiocyanate, which enhances Mn=CO π-bonding in the complex. In $Cr(CO)_5NCS^-$ the extent of Cr=CO π-bonding, as evidenced by the positions of the CO stretching frequencies, is already considerable, and hence the metal may exhibit little tendency to bond to the more polarizable sulfur atom. Unfortunately, no data are available at present to check the validity of the above supposition.

In order to assess further the effect of the metal charge on the nature of M–CNS attachment, attempts were made to synthesize the iron derivative, $Fe(CO)_4(CNS)_2$. However, no thiocyanatocarbonyl complex could be isolated and characterized from three different reactions tried.

Studies on solutions of thiocyanatopentacarbonylmanganese(I) reveal that equilibria between the two linkage isomers are attained rapidly and are sensitive to the nature of the solvent employed. Perhaps the most striking example of solvent importance in stabilizing a given mode of manganese–thiocyanate attachment is the behavior of the complex in acetonitrile. Addition of CH_3CN promotes formation of the isothiocyanate whereas removal of the solvent affords the S-bonded complex. These and previously mentioned observations (*vide supra*) indicate that the energy difference between the two isomers is indeed very small.

It is of interest to note that the isomerization of some saturated organic thiocyanates proceeds more readily in acetonitrile than in less polar solvents such as benzene and methyl ethyl ketone.[33] Although close analogy between these and our results is not justified—the former is a kinetic and the latter a thermodynamic effect—it is possible that mechanistically the rearrangements in acetonitrile are similar, and most probably involve ionization followed by a recombination of the ions. The conductivity data on $Mn(CO)_5NCS$ solutions are consistent with the presence of ionic species; however, this does not preclude other mechanisms, for example, an intramolecular rearrangement.

Finally, a rather unusual feature in the spectrum of $Mn(CO)_5NCS$ in acetonitrile merits a brief comment. The $A_1{}^1$ stretching mode of the N-bonded isomer (Table I) also gives rise to an absorption at a considerably lower frequency (*ca.* 40 cm.^{-1}) than that of the halogenopentacarbonyl complexes.[31] Similar positions of this band in the spectra of the two linkage forms of $Mn(CO)_5CNS$ indicate that the Mn=CO(1) bond orders are comparable. No satisfactory explanation in terms of manganese–thiocyanate bonding is available for this phenomenon at present. Quantitative studies on the kinetics and mechanism of the isomerization and on the equilibria in solution, which are now in progress, may help to resolve the problem.

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CONTRIBUTION NO. 1777 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES, CALIFORNIA 90024

The Synthesis of 1-Thia-4-telluracyclohexane (1,4-Thiatellurane) and Four of Its Addition Compounds

BY J. D. McCULLOUGH

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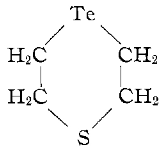
The previously unreported heterocyclic compound, 1-thia-4-telluracyclohexane, C_4H_8STe, has been synthesized by reaction of β,β'-dichlorodiethyl sulfide (mustard gas) with tellurium and sodium formaldehydesulfoxylate (rongalite) in aqueous solution. 1-Thia-4-telluracyclohexane is a white, crystalline solid (m.p. 69.5°) which forms crystalline addition compounds of the type $C_4H_8STeX_2$ with chlorine, bromine, and iodine, and a telluronium salt $[C_4H_8STeCH_3{}^+]I^-$ with methyl iodide.

An area of research under investigation in these laboratories involves synthetic, structural, and thermodynamic studies of the sulfur, selenium, and tellurium analogs of 1,4-dioxane.[1] The present paper describes the synthesis of 1,4-thiatellurane by reac-



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(1) J. D. McCullough, *Inorg. Chem.*, **3**, 1425 (1964), and references therein.