

TABLE I^a

Fe ^{II} complex	ν_6	ν_7	ν_8	Fe ^{III} complex	ν_6	ν_7	ν_8
Fe(CN) ₆ ⁻⁴	2040 s, br	584 s	417 m	Fe(CN) ₆ ⁻³	2042 w 2078 w 2118 s	510 w	390 s, br
Fe(CN) ₅ H ₂ O ⁻³	2015 w 2035 sh 2045 s } br	572 m	405 m 430 vw	Fe(CN) ₅ H ₂ O ⁻²	2070 w 2132 m	535 vw	400 s, br
Fe(CN) ₅ NH ₃ ⁻³	2000 sh 2040 sh } br	500 vw 566 s, br } 580 sh }	395 w 420 vw 435 vw	Fe(CN) ₅ NH ₃ ⁻²	2068 w 2123 s } 2140 m } 2150 m }	518 w	405 s, br 460 w
Fe(CN) ₅ NO ₂ ⁻⁴	2060 s, br	570 s	400 s, br } 425 sh }	Fe(CN) ₅ NO ₂ ⁻³	2065 w 2080 vw 2122 s } 2140 sh }	498 w	403 s, br
Fe(CN) ₅ SO ₃ ⁻⁵	2052 s, br	525 w 577 s	405 m } 435 sh }	Fe(CN) ₅ NO ⁻²	2148 s 2160 s 2170 s	470 w 497 w 515 vw	420 s } 435 sh } 450 sh }

^a s, strong; m, medium; w, weak; vw, very weak; br, broad. Infrared spectra were obtained by Beckman IR-7 and Carl Zeiss UR 10 infrared spectrometers for the NaCl and the KBr regions, respectively, using the Nujol mull technique.

increase of the metal-carbon σ -bond tends to increase both the MC and CN force constants and that the increase of the metal-carbon π -bond increases the MC force constant and decreases the CN force constant. By adding one $d\epsilon$ electron in passing from Fe(CN)₆⁻³ to Fe(CN)₆⁻⁴ there is apparently greatly increased M-C π -bonding leading to an increase in the MC force constant (ν_7 and ν_8 increase), a significant decrease in the CN force constant (ν_6 decreases), and to a considerable increase in change in CN bond moment accompanying the ν_6 vibration (the ν_6 peak absorption coefficient in aqueous solution increases 4.5 times).

Extending this interpretation to the Fe(CN)₅X complexes one concludes that the position of the MC and CN stretching bands and the shape of the latter indicate more π -bonding in the metal-carbon bond in Fe^{II} than in Fe^{III} pentacyano complexes. There appears to be some effect (weakening of the M-C π -bonding) when a CN⁻ group is replaced by an NO₂⁻ group. Nevertheless, the unusually high frequency and the shape of the CN band in Fe(CN)₅NO⁻² indicate less π -bonding in the M-C bond in this compound than in any other of the pentacyano complexes studied. This might be due, as has been pointed out by Ballhausen and Gray,¹ to the presence of "heavy M-NO π -bonding." The π -bonding is axially directed toward the NO group and the compound is by no means octahedral.⁶

There is another fact which adds evidence to the statement above: the ν_6 , ν_7 , and ν_8 bands are of the F_{1u} species, that is, triply degenerate. In passing to a lower symmetry one might expect the disappearance of the degeneracy and the splitting of the bands into their three components. This splitting has been observed for both CN and MC stretching bands⁷⁻⁹ in the case of

Fe(CN)₅NO⁻². However, there is no such pronounced splitting in the bands of the other compounds. With the exception of the ν_6 band of Fe(CN)₅NH₃⁻² one observes only the appearance of some fine structure in the CN band of some complexes that can be attributed to crystal effects.

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CENTRO BRASILEIRO DE PESQUISAS FÍSICAS
RIO DE JANEIRO
BRAZIL

LUCIA TOSI
J. DANON

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Thiocyanato-S-pentacarbonylmanganese(I) and Some Derivatives

Sir:

We wish to report the first simple thiocyanato metal carbonyl, Mn(CO)₅SCN, and to comment on the nature of attachment of the thiocyanate ion in this and some related compounds.

Thiocyanatopentacarbonylmanganese(I) is prepared by addition of a tetrahydrofuran solution of NaMn(CO)₅ to a stoichiometric amount of chlorothiocyanogen (ClSCN) in tetrahydrofuran under nitrogen. After removal of the solvent under reduced pressure, the residue is extracted with chloroform and filtered. Slow addition of petroleum ether to the filtrate affords golden yellow crystals (70–80% yield). The compound, which is a nonelectrolyte in nitromethane, dissolves readily in chloroform, acetone, acetonitrile, and methanol but not in benzene, petroleum ether, carbon

(6) There is the same evidence of π -bonding in the study of MC stretching mode in the Raman spectrum (H. Stammreich, private communication).

(7) F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).

(8) G. Bor, *ibid.*, **17**, 174 (1961).

(9) F. A. Miller, G. L. Carlson, F. F. Bentley, and W. H. Jones, *Spectrochim. Acta*, **16**, 135 (1960).

tetrachloride, and water. It is diamagnetic and relatively stable in the absence of light and under nitrogen. *Anal.* Calcd for $\text{Mn}(\text{CO})_5\text{SCN}$: C, 28.47; N, 5.53; S, 12.67; Mn, 21.70; mol. wt., 253. Found: C, 28.04; N, 5.50; S, 12.55; Mn, 21.60; mol. wt. (cryoscopic in nitrobenzene), 247, 259.

Infrared spectroscopic evidence serves to indicate the manner of attachment of SCN to the manganese. In addition to the stretching absorptions at 2135 cm^{-1} (m) (CN), 2110 cm^{-1} (w), 2060 cm^{-1} (s), and 1960 cm^{-1} (s) (CO) (chloroform solution), the compound shows a band at 676 cm^{-1} (Nujol), which is assigned to the CS stretching mode. Since the known S-bonded thiocyanates absorb between 690 and 720 cm^{-1} and N-bonded thiocyanates between 780 and 860 cm^{-1} ,¹ the band at 676 cm^{-1} indicates the presence of a Mn-SCN linkage in the compound.

Reactions of $\text{Mn}(\text{CO})_5\text{SCN}$ with a variety of neutral ligands yield complexes which are analogous to those prepared from $\text{Mn}(\text{CO})_5\text{Br}$.^{2,3} The derivatives⁴ *cis*- $\text{Mn}(\text{CO})_3(\text{py})_2\text{NCS}$ (py = pyridine), *cis*- $\text{Mn}(\text{CO})_3\text{-bipyNCS}$ (bipy = 2,2'-bipyridine), *cis*- $\text{Mn}(\text{CO})_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)_2\text{NCS}$, and *trans*- $\text{Mn}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{NCS}$ exhibit a band in the $780\text{--}860\text{ cm}^{-1}$ region and are therefore assigned thiocyanato-N structures. The same complexes may be obtained from the reaction of the corresponding chlorocarbonyl derivatives and potassium thiocyanate. Unlike the above compounds,

(1) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

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

(3) R. J. Angelici, F. Basolo, and A. J. Poë, *Nature*, **195**, 993 (1962).

(4) *cis* and *trans* refer to mutual positions of the two neutral ligands, *e.g.*, py. These are *cis* to SCN in both forms.

cis- $\text{Mn}(\text{CO})_3[\text{Sb}(\text{C}_6\text{H}_5)_3]_2\text{SCN}$ appears to contain S-bonded thiocyanate.

Turco and Pecile¹ made an interesting observation that, for Pt(II) and Pd(II) complexes, the nature of metal-thiocyanate attachment depends on the other ligands present. Good π -bonding ligands favor M-NCS linkage, whereas non- π -bonding ligands prefer a M-SCN bond. This approach has been successfully employed in the synthesis of thiocyanato-N and -S isomers.⁵

The preliminary experiments on manganese carbonyl systems prompt us to suggest that, in the presence of strongly π -bonding ligands (*e.g.*, CO), the effective charge on the metal may play an important role in determining the nature of the linkage isomer obtained. Thus, complexes containing bases weaker than $\text{P}(\text{C}_6\text{H}_5)_3$ (CO, $\text{Sb}(\text{C}_6\text{H}_5)_3$) are S-bonded, whereas complexes containing $\text{P}(\text{C}_6\text{H}_5)_3$ and stronger bases such as amines (py, bipy, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) are N-bonded. The generality of this statement and a possible explanation must await further experiments, which are now in progress.

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(5) F. Basolo, J. L. Burmeister, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

ANDREW WOJCICKI
MICHAEL F. FARONA

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Book Reviews

Advances in Fluorine Chemistry. Volume 3. Edited by M. STACBY, University of Birmingham, J. C. TATLOW, University of Birmingham, and A. G. SHARPE, Cambridge University. Butterworth, Inc., 7235 Wisconsin Avenue, Washington 14, D. C., 1963. 287 pp. $15.5 \times 25\text{ cm}$. Price, \$9.95.

Volume 3 of this series, well known to "fluorine chemists," continues the high standards of the two earlier works. The chapters are written by experts who speak with authority about their topics. They have reviewed various areas of current interest with thorough coverage of the literature so that the reader can get an up-to-date understanding of each topic. The book is intended primarily for persons engaged in research on compounds of fluorine.

The specific topics covered are indicated by the titles of the chapters: (1) Effects of Adjacent Perfluoroalkyl Groups on Carbonyl Reactivity, by H. P. Braendlin and E. T. McBee, Purdue University; (2) Perfluoroalkyl Derivatives of the Elements, by H. C. Clark, University of British Columbia; (3) Mechanisms of Fluorine Displacement, by R. E. Parker, University of Southampton; (4) Nitrogen Fluorides and Their Inorganic Derivatives, by C. B. Colburn, Rohm and Haas Company; (5) The Organic Fluorochemicals Industry, by J. M. Hamilton, Jr., E. I. du Pont de Nemours and Company; (6) The Preparation of Organic Fluorine Compounds by Halogen Ex-

change, by A. K. Barbour, L. J. Belf, and M. W. Buxton, Imperial Smelting Corp., Ltd.

The fifth chapter is written in a way which helps the research chemists to understand something about the organic fluorochemicals industry. The reviewer found it to be both interesting and informative.

In recent years it has become increasingly apparent that the words "fluorine chemistry" do not mean the same thing to all chemists working in the field. Since most of the research on fluorides deals with organic compounds, there is a tendency for some people to think only of such substances when the words are used. An illustration of this point of view may be found on p. 122 in the statement, "This then was the general state of fluorochemistry in 1928, when it was suddenly swept into its industrial phase by the rapidly expanding field of mechanical refrigeration." Obviously this statement does not apply to the fluorochemicals industries which were in operation before 1928. The confusion of meanings could be relieved by a more extensive use of words such as "organofluorine chemistry" or "organic fluorine chemistry." Editors can be helpful by encouraging such a practice.

This book is highly recommended reading matter for "fluorine research chemists."

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

GEORGE H. CADY