For a symmetry of D_{3h}, there should be three ν(Fe–C) and δ(Fe–C–O) infrared-active bands (Table II). In Table I, the position of these three bands has been given. No extra band has been found for the Fe–P stretching mode.

The $Mo(CO)_5 \cdot L$ complexes with a C_{4v} symmetry are expected[8] to have seven bands due to the Mo–C stretching and the Mo–C–O bending vibrations (Table II). As can be seen from Table I, seven such bands have been located experimentally.

Metal–Ligand Vibrations.—In both of the cases of iron and molybdenum carbonyl complexes no metal–ligand vibrations have been observed in the region studied. Other authors[11–13] have reported metal–P and metal–As vibrations in the R_3P and R_3As–metal halide complexes in the region 200–550 cm^{-1} (R stands for alkyl or aryl groups). In these cases there is no definite relationship between the vibrational frequency and the atomic mass of the metal. The only information available to the best of the authors' knowledge in the literature about the metal–P or metal–As vibrations in the R_3P- or R_3As-substituted metal carbonyl complexes is that of ν(Ni–P) at ~192 cm^{-1} in $Ni(CO)_3 \cdot LP$[14] and at 262 cm^{-1} in $Ni(CO)_3 \cdot PF_3$[7] complexes and of ν(Ni–As) at 207 cm^{-1} in $Ni(CO)_3 \cdot LA$[8] complexes. No explanation has been given for the apparent lowering of the Ni–P and Ni–As frequencies when the nickel carbonyl complexes are compared with the nickel halide complexes. A complete absence of the metal–N vibration in $M(CO)_5 \cdot CH_3CN$ complexes has recently been reported by Farona, *et al.*[15] No Mo–P vibration has been reported in $Mo(CO)_5R_3P$ complexes in earlier studies.[16]

Various reasons can be suggested for the absence of the metal–ligand bands in the infrared region studied for the metal carbonyl complexes, $M(CO)_xL_y$. Although a possibility, it seems highly improbable that both the M–P and M–As bands might be accidentally degenerate with the ν(M–C), δ(M–C–O), or the ligand vibrations in both the iron and molybdenum carbonyl complexes. The surrounding carbonyls also would not seem to decrease the M–L force constants so as to lower the energy of the vibration below 200 cm^{-1}; on the other hand, because of the strongly polarizing nature of the carbonyls, the metal–ligand force constant must be greater for metal carbonyls than for the metal halide complexes. We therefore believe that the absence of the metal–ligand vibrations in the substituted iron and molybdenum carbonyl complexes is probably due to the ν(M–L)–ν(M–C) coupling which renders ν(M–L) unobservable in the infrared region studied.

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Polarographic Characterization of Monocyano- and Monothiocyanatochromium(III) Complexes

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Both sulfur- and nitrogen-bonded thiocyanate complexes of chromium(III) have been reported[1] in connection with inner-sphere reduction of $Co(en)_2(NCS)X^+$ and $FeNCS^{2+}$ by Cr^{2+}. Linkage isomers of cyanochromium(III) have been proposed[2] as intermediate and product of the reaction of $Co(NH_3)_5CN^{2+}$ with Cr^{2+}. We have studied the polarographic properties of $CrNCS^{2+}$, $CrSCN^{2+}$, and $CrCN^{2+}$. Experiments designed to detect $CrNC^{2+}$ were not successful.

Experimental Section

Analytical grade reagents and water triply distilled from quartz were employed. $CrSCN^{2+}$ was prepared by reduction of $FeNCS^{2+}$ with Cr^{2+} in cooled solution and separated from other chromium species (except for $CrNCS^{2+}$) on a Dowex 50W-X8 column as described by Haim and Sutin.[1] The stock solution was kept frozen. Fresh solutions were prepared for each set of experiments. Solutions of $CrSCN^{2+}$ always contained about 30% $CrNCS^{2+}$.

$CrNCS^{2+}$ was prepared by heating stoichiometric amounts of $Cr(ClO_4)_3$ and NaSCN in solution and separating Cr^{3+} products on a Dowex 50W-X8 column.[3] Another method employed for preparation of $CrNCS^{2+}$ was the Cr^{2+}-catalyzed reaction of $Cr(ClO_4)_3$ with NaSCN.[4] Each species was analyzed for chromium after oxidation by hydrogen peroxide in alkaline solution. Thiocyanate was determined polarographically[5] after hydrolysis of the complex in alkaline solution. $[Co(NH_3)_5CN](ClO_4)_2 \cdot 0.5H_2O$ was prepared by the method of Siebert.[6]

$CrCN^{2+}$ was prepared by reduction of $Co(NH_3)_5CN^{2+}$ by Cr^{2+} in acidic solution and separated from Cr^{3+} and Co^{2+} by slow elution from Dowex 50W-X8 by 0.01 *M* $HClO_4$ in 1 *M* $NaClO_4$.[1] The species separated has a visible spectrum identical with that reported by Espenson and Birk[2] for $CrCN^{2+}$. A band of intensity similar to that of the first visible band (527 mμ) was observed at approximately 265 mμ, immediately followed by a very intense charge-transfer band.

Spectrophotometric measurements were made using the Cary 14. A Sargent XV polarograph was used for recording current–voltage curves. The capillary employed had a drop time of 3.4 sec and flow rate of 2.05 mg/sec (in short circuit with sce and 64-cm Hg column). A modified Kalousek polarographic cell was used. Potentials are listed in volts *vs.* the saturated calomel electrode. For investigation of positive anodic waves, however, the mercurous sulfate reference electrode was used. Ionic strength was adjusted to 1 *M* with $NaClO_4$.

Results

$CrNCS^{2+}$.—In acidic solutions this complex exhibits a polarographic wave corresponding to the reduction

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[1] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

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[5] SCN^- exhibits an anodic wave corresponding to formation of a complex with Hg^{2+}: I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63**, 1405 (1941).

[6] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

of the species by one electron per particle. The current is directly proportional to the square root of the height of the mercury column and hence is diffusion controlled. The half-wave potential is −0.65 V both in acid and in acetate buffer. In basic solutions, however, the wave collapses. After reacidification of such solutions, the wave of $CrNCS^{2+}$ is no longer present but a more negative wave indicates hydrolysis of $CrNCS^{2+}$ to hydrolytic polymers of Cr(III). The hydrolysis product could not be eluted with 1 *M* $HClO_4$ from a Dowex 50W-X8 column. After hydrolysis, the solution gives an anodic wave of approximately the same height as the original wave of $CrNCS^{2+}$. This wave was identified as corresponding to the Hg^{2+} complex of the SCN^- liberated by hydrolysis.[5] $CrNCS^{2+}$ itself does not give an anodic wave corresponding to complex formation with Hg^{2+} although the binuclear complex $CrNCSHg^{4+}$ has been described.[1]

Logarithmic analysis of the shape of the wave of $CrNCS^{2+}$ according to Tomes[7] gave a straight line with slope 100 mV/log unit, which indicates that the wave is irreversible. The half-wave potential is slightly changed with excess of free ligand ($E_{1/2}$ = −0.685 V for 1 *M* NaSCN).

$CrSCN^{2+}$.—The metastable isomer is polarographically reduced in the absence of free NCS^- with a half-wave potential of −0.35 V. The current corresponds to the reduction by one electron and is diffusion controlled. As in the case of $CrNCS^{2+}$, logarithmic analysis gives a straight line of slope 110 mV/log unit.[8]

The half-wave potential does not depend on pH of the solution, in solutions of pH 2.5 and higher, however, the cathodic wave disappears and a wave corresponding to reduction of $CrNCS^{2+}$ is formed. The original positive wave of $CrSCN^{2+}$ does not reappear if the solution is reacidified. In even more basic solutions, hydrolysis takes place as described in the case of $CrNCS^{2+}$. $CrSCN^{2+}$ does not exhibit an anodic wave. The cathodic waves of both $CrNCS^{2+}$ and $CrSCN^{2+}$ are complicated by maxima which may be easily suppressed by Triton X-100.

$CrCN^{2+}$.—This ion is reduced at the dropping-mercury electrode in a polarographic wave corresponding to a one-electron reduction. The half-wave potential is −0.96 V. The reduction wave is complicated by a maximum. Current at the maximum does not depend on the height of the mercury column. The maximum exhibits hysteresis, being more pronounced when scanning from positive to negative potentials. The maximum can be suppressed by Triton X-100. Neither the shape of the wave nor the half-wave potential depends on pH of the solution. In basic solutions, however, the reduction wave collapses while being shifted to more negative potentials. In very acidic solutions, slow hydrolysis occurs.

$Co(NH_3)_5CN^{2+}$.—This ion is reduced in a pH-independent one-electron reduction with half-wave potential of −0.36 V in buffered acidic solutions. The wave collapses in basic solution. In the absence of buffering, complications due to release of basic ligands near the electrode occur.

Discussion

In the presence of an equivalent concentration of NCS^-, Cr(II) gives an anodic wave close to the potential of the cathodic wave of $CrSCN^{2+}$. Both waves move to anodic potential as $[NCS^-]$ is increased.[8] Any cathodic current which might arise from reduction of $CrSCN^{2+}$ at more anodic potentials would be canceled by oxidation of the Cr(II) produced to $CrNCS^{2+}$. Since $CrSCN^{2+}$ is the less stable isomer, the occurrence of its reduction wave at more positive potentials than that of $CrNCS^{2+}$ is expected. This expectation also agrees with the tendency toward a positive correlation between more negative $E_{1/2}$ and lower wavelength of absorption for $Cr(H_2O)_5X^{2+}$ complexes (Table I). On the basis of these two factors, one would expect that $CrNC^{2+}$ would have an $E_{1/2}$ at a potential somewhat more positive than −0.9 V.

TABLE I

POSITION OF FIRST VISIBLE ABSORPTION BAND AND $E_{1/2}$, FOR SOME $Cr(H_2O)_5X^{2+}$ IONS AT 23°

X^-	λ_{max}, mμ	$-E_{1/2}$, V
$-I^-$	650	0.35[a]
$-Br^-$	622	0.37[a]
$-SCN^-$	620	0.35
$-Cl^-$	609	0.54[a]
$-NCS^-$	570	0.65
$-NC^-$	545–560	Not obsd
$-CN^-$	525	0.96

[a] 25°, F. J. Gomba and J. E. Earley, to be published.

Espenson and Birk[2] have observed two slow steps in the spectrophotometric study of the reduction of $Co(NH_3)_5CN^{2+}$ with Cr^{2+}. They prefer the mechanism

$$Co(NH_3)_5CN^{2+} + Cr^{2+} + 5H^+ \xrightarrow[\text{rapid}]{k} Co^{2+} + 5NH_4^+ + CrNC^{2+}$$

$$CrNC^{2+} \xrightarrow[\text{slow}]{k'} CrCN^{2+}$$

where *k* is 61 ± 6 M^{-1} sec^{-1} and *k'* is 9.2×10^{-3} sec^{-1} at 15°. We have attempted to detect the proposed intermediate $CrNC^{2+}$, polarographically.

The rate of destruction of Cr^{2+} was followed by recording the decrease of anodic current of Cr(II) at −0.25 V, at which potential $Co(NH_3)_5CN^{2+}$ does not interfere. These measurements were consistent with a second-order reaction with a rate constant at 15° close to 60 M^{-1} sec^{-1}. Kinetic runs at more negative potentials gave similar results; in no case was any electroactive species, other than Cr^{2+}, $Co(NH_3)_5CN^{2+}$, or $CrCN^{2+}$, detected. Formation of a wave at −0.96 V, which corresponds to $CrCN^{2+}$, was completed in times of the order of 1 min. No change in polarographic properties was noted for the succeeding 10 min.

Although the $CrNC^{2+}$ would be expected to be reduced at potentials more positive than −0.9 V, no

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[7] J. Tomes, *Collection Czech. Chem. Commun.*, **9**, 12 (1937).

[8] Addition of free NCS^- causes the wave to move to more negative potentials. F. Anson and E. Passeron (private communication) have observed a parallel effect of SCN^- on the oxidation of Cr(II).

such reduction wave was observed. There are a number of ways by which $CrNC^{2+}$ could escape polarographic detection, for instance, reoxidation of the reduction product of $CrNC^{2+}$ to $CrCN^{2+}$ could cancel the wave of $CrNC^{2+}$.

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The Synthesis of 1,2-Benzocycloheptatrieneiron Tricarbonyl and Benzotropeniumiron Tricarbonyl Tetrafluoroborate

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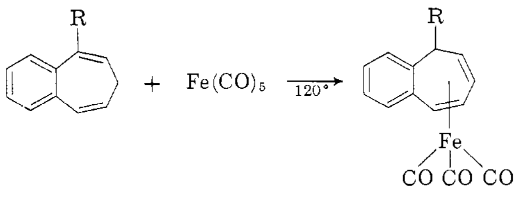
The tendency for iron to form tricarbonyl complexes with conjugated dienes leads to an interesting question as to the products which would arise from the reaction of 3,4-benzocycloheptatriene with iron pentacarbonyl. There are no examples of an iron carbonyl fragment complexed to a benzenoid aromatic system. The nonbenzenoid aromatic hydrocarbon azulene does form a diiron pentacarbonyl derivative.[1] However, crystal structure data indicate that the π electrons of the five- and seven-membered rings of azulenediiron pentacarbonyl are localized within the respective rings.[2] Isomerization of the 3,4-benzocycloheptatriene to the 1,2-benzo isomer in the presence of iron pentacarbonyl would lead to a simple diene which would be expected to form a tricarbonyl complex. This latter path is correct as evidenced by the facile reaction of both 3,4-benzocycloheptatriene and 5-methyl-3,4-benzocycloheptatriene with iron pentacarbonyl at 120° to yield 1,2-benzocycloheptatrieneiron tricarbonyl (**1**) and 7-methyl-1,2-benzocycloheptatrieneiron tricarbonyl (**2**), respectively.



1, R = H
2, R = CH_3

The structures can be verified by the nmr spectra of the compounds. The nmr spectrum of 1,2-benzocycloheptatrieneiron tricarbonyl (**1**) is shown in Figure 1. The two-hydrogen multiplet at τ 4.55 is assigned to the 4,5 hydrogens and the two multiplets at τ 6.2 and 6.6 are assigned to the 3 and 6 hydrogens, respectively. The assignments are based on the generally observed chemical shifts of cyclic dieneiron tricarbonyls.[3] The alternate structure of 3,4-benzocycloheptatrieneiron tricarbonyl is excluded by the nmr spectrum since this latter structure should exhibit only two types of vinyl hydrogens. The assigned structure for 7-methyl-1,2-benzocycloheptatrieneiron tricarbonyl is established by the similarity of the nmr spectrum to that of 1,2-benzocycloheptatrieneiron tricarbonyl and the fact that the methyl appears as a doublet (J = 6.7 cps).

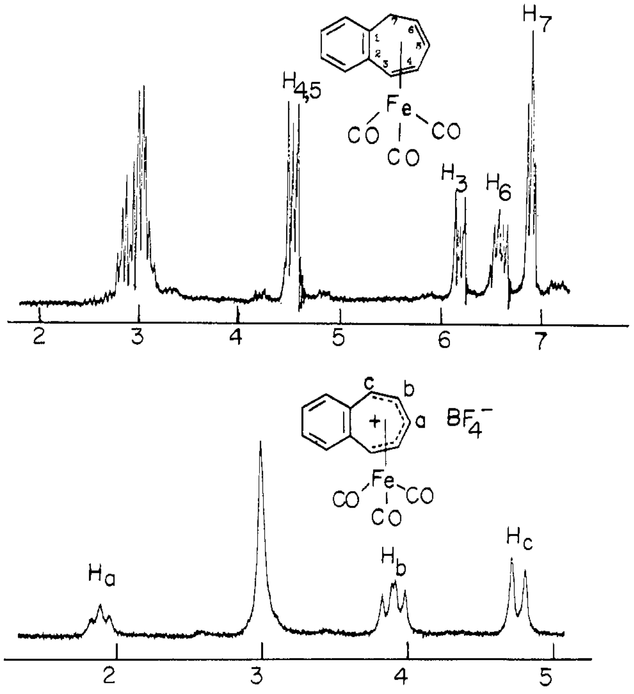


Figure 1.—Nmr spectrum of 1,2-benzocycloheptatrieneiron tricarbonyl.

The fact that cycloheptatrieneiron tricarbonyl will not undergo hydride abstraction when treated with triphenylcarbonium tetrafluoroborate, but reacts by addition instead,[3,4] can be explained by the preference of the iron tricarbonyl group to favor a pentadienium ion ligand which has an empty nonbonding π orbital available for back bonding, rather than a tropenium ion ligand which has only unfilled antibonding π orbitals.[5] However, 1,2-benzocycloheptatrieneiron tricarbonyl (**1**) could undergo hydride abstraction to give a complex more nearly resembling a benzenepentadienium ligand with little interaction between the benzene and pentadienium π systems rather than one electronically resembling a benzotropenium ligand. Treatment of 1,2-benzocycloheptatrieneiron tricarbonyl with tri-

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