TABLE I

EXCHANGE OF CHROMIUM(II) ION AND *cis*-DIAZIDOTETRAAQUOCHROMIUM(III) ION AT 0° AND $I \cong 0.5\ M$

| $[H^+]$ | $[Cr^{2+}] \times 10^3$ | $[Cr(N_3)_2^+] \times 10^3$ | $t_{1/2}$, sec. | $k$,[a] l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|
| 0.4 | 2.4 | 0.74 | 3.9 | 57 |
| .4 | 1.16 | 0.74 | 6.0 | 61 |
| .45 | 0.77 | 1.39 | 5.3 | 60 |
| .85 | 0.78 | 1.20 | 5.1 | 68[b] |

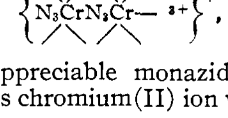
[a] $k = 0.69/([Cr^{2+}] + [Cr(N_3)_2^+])t_{1/2}$. [b] $I \cong 0.9\ M$.

conformed to the usual exponential approach to random mixing of chromium-51 between the chromium species, it can be concluded that this reaction goes *via* a double-bridged transition state.

In addition to several single point experiments which demonstrated exchange, four kinetic experiments involving several points were run. These experiments are summarized in Table I. The second-order rate coefficient for exchange *via* the double-bridged transition state, $k \cong 60$ l. mole$^{-1}$ sec.$^{-1}$ at 0° and an ionic strength of $\sim 0.5$ molar, is considerably larger than the value $k \cong 1.3$ l. mole$^{-1}$ sec.$^{-1}$ for exchange of monazidochromium(III) ion and chromium(II) ion under these same conditions.[5] The mild increase in rate with a two-fold increase in hydrogen ion concentration can be attributed to the increase of electrolyte concentration.

Although the factors responsible for greater stability of the transition-state involving bridging by two azide ions relative to that with a single bridging azide ion, in contrast to the reverse situation for fluoride ion or water acting as bridging groups, are not obvious, both the electronic structure of azide ion, with its pi bonding, and steric considerations may be relevant. Without great strain, appropriate values for the Cr–N–N angle would be accessible to form a symmetrical double-bridged transition-state.

Diazidotetraaquochromium(III) ion was prepared by oxidation of chromium(II) ion with a large excess of azide ion[6] present as a sodium azide–hydrazoic acid buffer (0.1–0.2 $M$ in each constituent). Product species of charge +1, the isomeric diazidochromium(III) ions, were separated from reaction products of higher charge (monoazidochromium(III) ion, aquochromium(III) ion, and amminochromium(III) species[3]) by ion-exchange. At the electrolyte concentrations employed, ions of charge +1 pass directly through the column. After freeing this solution of uncomplexed azide by acidification and aeration with nitrogen, it was treated with chromium(II) ion. This procedure, designed to convert *trans* diazidochromium(III) ion to monoazidochromium(III) ion *via* a transition state



$$\left\{ N_3CrN_3Cr— {}^{3+} \right\}^{\ddagger},$$

did produce appreciable monazidochromium(III) ion. The excess chromium(II) ion was treated with iron(III) ion or oxygen, and residual diazidochromium(II) ion, presumably the *cis* isomer, was separated from other chromium and iron species by ion-exchange. Analysis of two independent batches of complex prepared in this way gave values of azide/chromium of 1.96 and 2.14.

Aliquots of reaction mixture in kinetic experiments were quenched into a dilute solution of hydrogen peroxide at 4–5 times ranging from 3 to 18 seconds after mixing. Diazidochromium(III) ion, the only chromium species of charge +1 in the quenched solution was separated from other chromium species by ion-exchange. Visual inspection of the column containing light colored ion-exchange resin showed no detectable monazidochromium(III) ion. An analysis for chromium(II) ion performed at the end of each experiment corresponded closely to the amount added.

The fraction exchange was calculated using either a directly measured infinity-time specific activity or a value calculated from the specific activity of the chromium(II) ion and the solution composition. In two experiments, an appreciably better correlation of data was obtained using the former quantity.

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## BRIDGE ADDUCTS—THE INTERACTION OF $BF_3$ WITH TRANSITION METAL CYANIDE COMPLEXES

*Sir:*

This communication reports the general Lewis basicity of some transition metal cyanide complexes. One example of this phenomenon is afforded by the compounds formed between boron trifluoride and $K_2Ni(CN)_4$. Spectral evidence, stoichiometry of formation, and magnetic data indicate the presence of cyanide bridges (*e.g.*, —Ni—C≡N—$BF_3$) in this new class of compounds.

Potassium tetracyanonickelate(II)[1] was dried by heating the solid under high vacuum (less than $10^{-4}$ mm.); and boron trifluoride addition was accomplished by three methods. (1) It was found that purified $BF_3$[2] at a pressure of *ca.* 50 mm. slowly added to $K_2Ni(CN)_4$ which was maintained at 85°. After about two hours absorption appeared to slow down.[8] In a typical run 1.30 millimoles of $K_2Ni(CN)_4$ absorbed 1.29 millimoles of $BF_3$ (as indicated by $P$, $V$ and $T$ measurement of $BF_3$); also weight increase of the solid corresponded to an uptake of 1.28 millimoles $BF_3$. (2) A 1:1 adduct also was obtained by the interaction of dry $K_2Ni(CN)_4$ with an excess of practical grade 47% boron trifluoride etherate. The infrared spectrum and color of this product indicated it was less pure than that produced by procedure one. (3) Boron trifluoride at greater than one atmosphere pressure was allowed to react with $K_2Ni(CN)_4$ in a sealed glass tube for two weeks at room temperature.

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(5) R. Snellgrove and E. L. King, forthcoming publication.

(6) With only an equivalent amount of azide present at much lower concentrations, the reaction products include chromium(III)-ammine species (M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962)).

(1) $K_2Ni(CN)_4$ was prepared by the method of W. C. Fernelius and J. J. Burbage, *Inorg. Syntheses*, **2**, 227 (1946).

(2) H. C. Brown and R. B. Johannsen, *J. Am. Chem. Soc.*, **72**, 2937 (1950).

The product of this reaction contained four moles of $BF_3$ for each mole of $K_2Ni(CN)_4$.

Failure to obtain X-ray diffraction patterns from the foregoing compounds indicates an amorphous structure. Solvents ($H_2O$, acetone, dimethyl sulfoxide, dimethylformamide, nitrobenzene, ethers and ethyl alcohol) either fail to dissolve the adduct or bring about decomposition. Furthermore, even brief contact with atmospheric moisture results in partial decomposition.

Despite the foregoing experimental difficulties, it was possible to obtain fairly conclusive structural evidence. The infrared spectrum of pure potassium tetracyanonickelate(II) displays a single absorption at 2130 cm.$^{-1}$. This band represents the degenerate $C\equiv N$ stretch for the square planar array of terminal cyanides coördinated to nickel. By contrast, the compound $K_2Ni(CN)_4 \cdot 4BF_3$ yields a single absorption (2250 cm.$^{-1}$) which is over 100 wave numbers higher than that of the parent $K_2Ni(CN)_4$. For the intermediate compound, $K_2Ni(CN)_4 \cdot BF_3$, infrared absorption in the $C\equiv N$ stretch region consists of one band at 2127 cm.$^{-1}$ and another at 2235 cm.$^{-1}$. It thus appears logical to assign the 2127 cm.$^{-1}$ absorption primarily to stretching frequencies of terminal cyanides and the 2235 cm.$^{-1}$ band primarily to the stretching frequency of $C\equiv N$ in a bridge environment ($-Ni-C\equiv N-BF_3$). Significantly, the frequency region assigned to the bridge cyanide stretch is well outside the reported range of Raman active non-degenerate modes for $Ni(CN)_4$: 2149 and 2160 cm.$^{-1}$.[3] The shift of $C\equiv N$ stretch to higher frequencies upon bridge formation is in keeping with observations on boron trihalide-nitrile systems[4] and transition metal cyanide bridged compounds.[5]

If the infrared and stoichiometry data were taken without reference to the nitrile–$BF_3$ and cyanide bridged metal complexes, a good case could be made for abstraction of $C\equiv N^-$ from the first coördination sphere of nickel by $BF_3$. However, the possibility of a large change in the first coördination sphere of nickel, which would occur upon $C\equiv N^-$ abstraction, is effectively ruled out by the similarity of color and electronic spectra of $K_2Ni(CN)_4$, $K_2Ni(CN)_4 \cdot BF_3$ and $K_2Ni(CN)_4 \cdot 4BF_3$. A similar conclusion may be derived from the observed diamagnetism of both $K_2Ni(CN)_4 \cdot BF_3$ and its parent $K_2Ni(CN)_4$.

The reflectance spectrum of another $BF_3$ adduct, $K_4Mo(CN)_8 \cdot 7.3BF_3$, displays a broad maximum at 365 m$\mu$ (27,400 cm.$^{-1}$) and a shoulder at *ca.* 415 m$\mu$ (24,100 cm.$^{-1}$). These bands agree within experimental error with those of $K_4Mo(CN)_8$. Again, it is inferred that addition of $BF_3$ leaves the first coördination sphere of the metal unchanged. This is consistent with simple addition of $BF_3$ to the nitrogen end of cyanide groups. Lower frequency infrared bands for the above compounds also agree with the proposed bridge structures. Upon coördination $BF_3$ assumes a pyramidal configuration which should display symmetric and asymmetric stretching frequencies; also a B–N stretch frequency should appear in the NaCl infrared region. In harmony with these expectations, a broad intense maximum about 1100 cm.$^{-1}$, another around 900 cm.$^{-1}$ and a weak maximum near 700 cm.$^{-1}$ are observed with all of the compounds reported.

Preparation of the bridge adducts, $K_2Ni(CN)_4 \cdot 4BF_3$, $K_4Fe(CN)_6 \cdot 3.7BF_3$ and $K_4Mo(CN)_8 \cdot 7.3BF_3$, demonstrates the generality of Lewis base behavior by metal cyanide complexes. Lack of simple $BF_3$-metal cyanide ratios for some of the above compounds is attributed to the kinetically unfavorable situation of solid–gas reactions involved in their formation. In all of these cases bridge formation is accompanied by the appearance of new $C\equiv N$ stretch absorptions at higher frequencies than found in the original nonbridged complex. Evidence for a $BH_3$ adduct of $K_4Fe(CN)_6$ also has been obtained. The scope of bridge adduct formation found in the present work makes a bridge structure plausible for the compound $AgCN \cdot BBr_3$.[6]

The compounds produced in this study are remarkably stable with respect to evolution of $BF_3$. For example a 0.9 millimole sample of $K_4Mo(CN)_8 \cdot 1.2BF_3$ was subjected to a vacuum of less than $10^{-4}$ mm. for one hour at a temperature of 32°, but less than $2 \times 10^{-3}$ millimole of condensables was collected. This behavior contrasts sharply with observations that benzonitrile–$BF_3$ would exert a boron trifluoride pressure of 3.1 mm. at 32°,[2] while acetonitrile–$BF_3$ would exert a $BF_3$ pressure of 6.2 mm. at this temperature.[7] The origin of this great stability is one aspect of bridge adduct formation currently under investigation.[8]

This research was supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

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[3] J. P. Mathieu and S. Cornevin, *J. Chim. Phys.*, **36**, 271 (1939). If the $C\equiv N—BF_3$ group is approximated as a cylindrically symmetrical "ligand" the square planar $Ni(CN)_4 \cdot BF_3^{--}$ anion would have $C_{2v}$ symmetry and selection rules for the isolated ion would predict three infrared active modes in the terminal $C\equiv N$ stretch region. An effort was made to resolve the single 2127 cm.$^{-1}$ band using a Perkin Elmer 112 equipped with $CaF_2$ optics, but without success.

[4] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[5] D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. and Nucl. Chem.*, **21**, 33 (1961).

[6] E. Pohland, *Z. anorg. Chem.*, **201**, 282 (1931).

[7] A. W. Laubengayer and D. S. Sears, *J. Am. Chem. Soc.*, **67**, 164 (1945).

[8] Absorption rate experiments show no definite break at a 1:1 stoichiometry but under the proper conditions this composition is easily attained.

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## AN UNUSUAL INTRAMOLECULAR DIELS-ALDER REACTION IN THE PHOTOÖXIDATION OF A (FURANO) HETEROCYCLOPHANE

*Sir:*

The dye-sensitized photoöxidation of furans in reducing solvents such as methanol yields, among other products, diacyl or diaroylethylenes as in the conversion of tetraphenylfuran to *cis*-dibenzoylstilbene.[1,2] Applied to the heterocyclophane I,[3]

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[1] H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.*, **82**, 2086 (1960).

[2] R. E. Lutz, W. J. Welstead, Jr., R. G. Bass and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962).

[3] H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theo-