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THE REACTION OF ACETYLENIC COMPOUNDS WITH HEXACYANODINICKELATE(I) ION IN AQUEOUS SOLUTION

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During the course of our studies (1) with d^7 transition metal complexes and acetylenic compounds, the reactions of potassium hexacyanodinickelate(I), $K_4Ni_2(CN)_6$, (2) were investigated. We now wish to report that aqueous solutions of $K_4Ni_2(CN)_6$ will oligomerize disubstituted acetylenic compounds at atmospheric pressure with ease. This novel result actually complements and extends former observations on the reactions of acetylenic compounds (3) and Ni(II) cyanide systems, but in some respects it is in sharp contrast to similar reactions (4) of d^7, $[Co(CN)_5]^{3-}$ which gives only trans-$[(CN)_5Co(CH_3O_2C{-}C{=}C{-}CO_2CH_3)Co(CN)_5]K_6$.

Thus blood red aqueous solutions of $K_4Ni_2(CN)_6$ at 25°C reacted exothermically with alcoholic solutions of dimethyl acetylenedicarboxylate (A) to give > 80% yields[†] of hexamethylmellitate, which was identified by mixed m.p. and spectral comparisons with an authentic sample. When a ten-fold or one-hundred fold excess of (A) was used, the yield of trimer was 99%, although to achieve this result it was necessary to heat the reaction mixture to 50°C. Trimerization of (A) may continue even after removal of the product. Thus the Ni(I) cyanide system is catalytic in its behavior, although it is eventually destroyed and Ni(II) cyanide can be isolated from the reaction mixture. However, as long as sufficient (A) was present in the system and the temperature was moderated, the catalyst system appeared to remain viable.

The solutions of $K_4Ni_2(CN)_6$ seem to be most effective catalytically with acetylenic compounds that have "electron-withdrawing" substituents. Thus hexyne-3 was least reactive and < 1% hexaethylbenzene was isolated from the reaction mixture. Furthermore, acetylenic compounds which are not soluble in water gave no evidence of reaction. The reaction with acetylene gas (5) yielded a thick dark brown to black mass in ½ hr; the isolated material had

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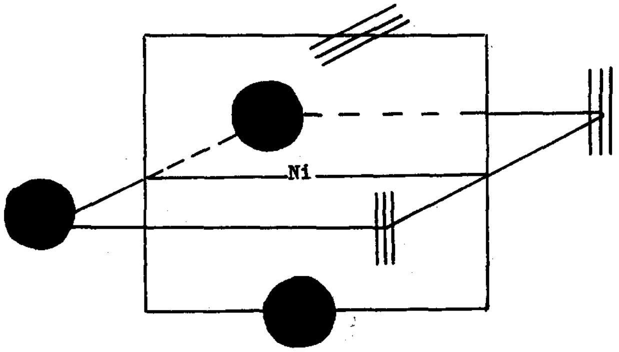
[†] Yields were calculated on the basis of dimethyl acetylenedicarboxylate

spectral properties which were similar to a linear acetylene polymer. No evidence for benzene or cyclooctatetraene was found. The presence of non-aqueous solvents such as tetrahydrofuran (THF) or ethanol severely limited the catalytic nature of $Ni_2(CN)_6^{4-}$. In the presence of acid the formation of trimer was drastically curtailed and reduction of (A) to dimethylfumarate and dimethylsuccinate was observed by vpc analysis of the reaction mixture.

A surprising observation was noted when the reaction mixture with (A) was filtered from the trimer and then added to a large volume of alcohol. A small amount of oil separated which slowly crystallized to a pale yellow, very hygroscopic solid (6). Anal. Calcd. for $[(CN)_3Ni(CH_3O_2C\text{-}C{=}C\text{-}CO_2OH_3)Ni(CN)_3]K_4 \cdot 2H_2O$. C, 23.70; H, 1.66. Found: C, 23.17; H, 1.92. An infrared spectrum of the solid in perfluorokerosene showed the presence of -OH stretching bands from coordinated water, C-H stretching absorptions, and a carbonyl peak at 1710 cm^{-1}. Additional bands at 2175, 2125, and 2100 cm^{-1} (KBr pellet) were observed, and assigned to $\nu_{C\equiv N}$ stretching frequencies. This is consistent with bands observed for the cobalt complex. The solid is very soluble in water. We were unable to obtain any organic derivative after treating a water solution of the yellow solid with I_2-I_3^-. It is not clear whether this nickel adduct is a precursor to the trimerization of the disubstituted acetylene or whether a coordinatively saturated complex as postulated by Schrauzer (7,8) is the active species,



Since we have found that CN^- is beneficial to the trimerization the formation of an active species may occur as follows (9):

$$Ni_2(CN)_6^{4-} + 2CN^- \rightleftarrows 2Ni(CN)_4^{3-}$$

$$Ni(CN)_4^{3-} + 3L \rightleftarrows Ni(CN)_3L_3^{2-} + CN^-$$

L = disubstituted acetylene

This proposal is further supported by the observation that paramagnetic nickel salts are the best catalytic agents (7), and the only way to form such a species from the diamagnetic $Ni_2(CN)_6{}^{4-}$ in solution is to promote cleavage by the disubstituted acetylene or CN^- to yield the paramagnetic d^7 or d^9 complex (10).

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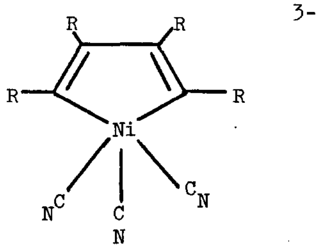
6. This yellow salt may actually be the remnant of a more reactive species, since attempts to react the material with more di-substituted acetylene have not been successful. Futhermore, higher molecular weight organic products such as R-CH=CR-CR=CH-R $(R=CH_3CO_2{}^-)$ have not been isolated. It is intriguing, however, to speculate that complexes such as



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10. It is perhaps a matter of speculation whether $[Ni_2(CN)_6]^{4-}$ is d^7 or d^9 in electronic structure, since the structure of the ion is not exactly clear.