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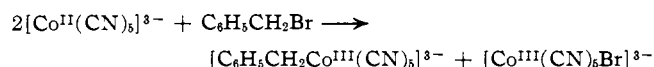
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Pentacyanobenzylcobaltate(III). A New Series of Stable Organocobalt Compounds

Sir:

We wish to report the preparation and characterization of a new series of stable, water-soluble organocobalt compounds, which are formed by the reduction of organic halides with pentacyanocobaltate(II).

On addition of benzyl bromide to a water-methanol solution containing CoCl_2 and NaCN (which react together to form $\text{Co}(\text{CN})_5^{3-}$)¹ in the absence of air, a compound which we are led to formulate as pentacyanobenzylcobaltate(III) is rapidly formed by the reaction



By fractional precipitation and recrystallization from alcohol solutions, the sodium salt of $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]^{3-}$ could be separated from the less soluble salts of $\text{Co}(\text{CN})_5\text{Br}^{3-}$, $\text{Co}(\text{CN})_5^{3-}$, and $\text{Co}(\text{CN})_5\text{OH}^{3-}$, which are by-products of the reaction. *Anal.* Calcd. for $\text{Na}_3[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$: Co, 15.3; C, 37.4; H, 2.9; N, 18.2. Found: Co, 15.8; C, 37.6; H, 3.2; N, 17.6. The original yield of $\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5^{3-}$, based on the ultraviolet spectrum of the reaction solution, is estimated to be about 70%.

$\text{Na}_3[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ is a yellow, somewhat deliquescent, crystalline salt. It is soluble in water, methanol, and ethanol and insoluble in ether, acetone, or hydrocarbons. Thermal decomposition *in vacuo* yields dibenzyl as the organic product. Alkaline aqueous solutions of $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]^{3-}$ are stable in the absence of oxygen and show no immediate reaction with NaBH_4 or CO . The anion is decomposed slowly by oxygen and rapidly by acids, the course of the latter reaction being complex and as yet unresolved. The ultraviolet and n.m.r. spectra of $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]^{3-}$ are summarized in Table I. The origin of

the intense band at 295.5 μm , which is not characteristic of other pentacyanocobaltate(III) complexes, is not clear but is believed to be connected with the aromatic component of the complex, since the corresponding alkyl complexes do not exhibit this band. The chemical shifts of the benzyl protons are similar to those observed in $\text{C}_6\text{H}_5\text{CH}_2\text{HgCl}$ (CH_2 , -1.85 ; C_6H_5 , -5.86 p.p.m. from *t*-butyl alcohol, measured in CDCl_3).

Pentacyanoalkylcobaltate(III) compounds may be similarly prepared although the study of these has not proceeded as far as that of the benzyl compound. The reaction of CH_3I with $\text{Co}(\text{CN})_5^{3-}$ yields $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ which has also been obtained, in nearly pure ($\sim 90\%$) form, as the sodium salt. The ethyl and *n*-propyl compounds can be similarly prepared in solution although these are less stable than the benzyl and methyl analogs and have not as yet been fully characterized or recovered in pure form. The ultraviolet spectrum of $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ resembles that of other typical pentacyanocobaltate(III) complexes, e.g., $[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$, and the band at 318 μm (whose counterpart in the benzyl compound presumably is obscured by the tail of the much more intense 295 μm band) may accordingly be assigned to a $(t_{2g})^5(e_g)^1 \leftarrow (t_{2g})^6$ transition. This suggests that the ligand field strength of CH_3 approaches that of CN^- (λ_{max} 311 μm for $\text{Co}(\text{CN})_5^{3-}$) and is in line with the high ligand fields exhibited by alkyl ligands in other complexes.² $[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$ reacts with HgCl_2 to form CH_3HgCl and with I_2 to form CH_3I .

The formation of a binuclear, unsaturated organopentacyanocobalt(III) complex, $[(\text{CN})_5\text{Co}-\text{CH}=\text{CH}-\text{Co}(\text{CN})_5]^{6-}$, by a somewhat different route, namely the reduction of acetylene by $\text{Co}(\text{CN})_5^{3-}$, has previously been described by Griffith and Wilkinson.³ The $[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]^{3-}$ anion and its alkyl analogs reported here are isoelectronic with the corresponding stable organomanganese pentacarbonyls, e.g., $\text{CH}_3\text{-Mn}(\text{CO})_5$; their mode of preparation, described above, finds an analogy in the formation of another stable, water-soluble organometallic complex, $[\text{C}_6\text{H}_5\text{CH}_2\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5]^{2+}$, by the reduction of benzyl chloride with chromium(II).⁴ Finally, reference should be made to some interesting points of analogy between the chemistry of $\text{Co}(\text{CN})_5^{3-}$, revealed here, and that of the reduced derivatives of vitamin B_{12} (*i.e.*, vitamins B_{12r} and B_{12s}), including the reactions of the latter with alkyl halides and other alkylating agents to form stable alkyl cobalt derivatives.⁵

Further studies on the preparation and characterization of these compounds are in progress.

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TABLE I

Anion	$\text{C}\equiv\text{N}$ stretching frequency, cm.^{-1} ^a	Ultraviolet absorption λ_{max} (ϵ_{max}), μm	Proton n.m.r. spectra in D_2O	Chemical shift, p.p.m. ^b
$[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CN})_5]^{3-}$	2093 ± 3	$295.5 (1.8 \times 10^4)$	CH_2 C_6H_5	-1.67 -6.01
$[\text{CH}_3\text{Co}(\text{CN})_5]^{3-}$	2094 ± 3	$318 (2.9 \times 10^2)$	CH_3	$+0.70$
$[\text{C}_2\text{H}_5\text{Co}(\text{CN})_5]^{3-}$ ^c	2094 ± 3	...	CH_2 CH_3	-0.35 $+0.09$

^a Measured on the sodium salt in KBr pellet. ^b Relative to *t*-butyl alcohol. ^c Based on impure samples.

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