Registry No. $(ET)_2ReO_4$, 87825-70-5; $(ET)_2BrO_4$, 89936-63-0.

Supplementary Material Available: Tables of final positional parameters and anisotropic temperature factors (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Carbonylpentacyanocobaltate(III)

Sir:

Most stable carbonyl complexes are formed with transition metals in a negative oxidation state or one of the lower oxidation states. A notorious exception is the carbonylpentacyanoferrate ion,[1] with iron in its +2 oxidation state. More recently the synthesis was reported of a binuclear Mn(III) complex in which two CO molecules act as bridging ligands.[2]

Because of our interest in the chemistry of various $Co^{III}(CN)_5X^{n-}$ complexes, the existence of the iron (+2) carbonyl compound prompted us to attempt the synthesis of the isoelectronic $Co(CN)_5CO^{2-}$ complex ion, in which the cobalt atom is formally in the +3 oxidation state.

Almost sixty years ago Manchot and Gall reported on the synthesis of what they believed to be the $K_3[Co(CN)_5CO]$ complex.[3] Hieber et al., however, have proved that the procedure of Manchot and Gall leads to a mixture of $K_3[Co(CN)_6]$ and $K[Co(CO)_4]$.[4] They also found that is was impossible to prepare the $K_2[Co(CN)_5CO]$ compound by interaction of CO with $Co(CN)_5OH_2^{2-}$ in aqueous solution.

Our first attempts to prepare $K_2[Co(CN)_5CO]$ in an analogous way as the complex $Na_3[Fe^{II}(CN)_5CO]$ were unsuccessful: as contrasted with the facile reaction of $Fe(CN)_5NH_3^{3-}$ with CO in aqueous solution[5] we did not observe any reaction for several $Co(CN)_5X^{n-}$ complexes (X = H_2O, NH_3, Cl^-).

However, in a carbon monoxide saturated methylene chloride solution various $(n\text{-}Bu_4N)_n[Co(CN)_5X]$ complexes undergo a thermal or photochemical substitution reaction yielding the desired $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ complex. For the sake of convenience we used the thermal reaction of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ with CO in CH_2Cl_2 at 298 K. The synthesis of the chloropentacyanocobaltate(III) complex was described earlier.[6] Prior to dissolution of the $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ complex the solvent was saturated with CO in order to avoid the eventually interfering dimerization reaction of the starting complex.[7] The initial concentration of the complex was between 10^{-3} and 10^{-2} M. The solution discolors within a few minutes. As can be seen in Figure 1, the ligand field band of the original species vanishes completely and a new band appears at 310 nm. During the reaction the absorption spectra in the UV region evolve over two isosbestic points.

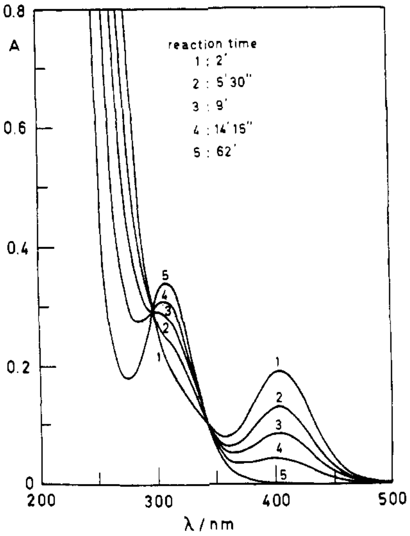

Figure 1. UV–visible spectra during the reaction of $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ with CO.

For the reasons enumerated below, we ascribe these spectral changes to the reaction

$$(n\text{-}Bu_4N)_3[Co(CN)_5Cl] + CO \rightarrow (n\text{-}Bu_4N)_2[Co(CN)_5CO] + (n\text{-}Bu_4N)Cl$$

The reaction product is isolated over Sephadex LH 20 from the released $(n\text{-}Bu_4N)Cl$ by elution with CH_2Cl_2. The new complex is then precipitated as fine white crystals by the addition of diethyl ether and dried in vacuo over P_2O_5. The ultimate yield is about 80% due to some loss on eluting the complex over Sephadex.

The formula $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ for the isolated product was first confirmed by analysis of the cobalt content. Our experimental value of 8.47% agrees very well with the theoretical value of 8.40%. An elementary C, N, H analysis of our product, however, appears to be not very relevant due to the presence of two $n\text{-}Bu_4N^+$ cations.[5] A second argument for the above formula stems from the determination of the Co/CO ratio in a ^{14}CO-labeled sample of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$. The Co/CO ratio was found to be 1.03/1.00. In addition we found that $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in aqueous acid solution was quantitatively converted by UV irradiation into the $Co(CN)_5OH_2^{2-}$ ion, thus confirming the presence of the $Co^{III}(CN)_5$ moiety in the new product.

We have repeated the synthesis with several acidopentacyanocobaltate(III) complexes as starting material. In some cases (e.g. Cl^-, N_3^-) the reaction runs thermally. Other complexes such as $(n\text{-}Bu_4N)_2[Co(CN)_5py]$ are thermally inert, but upon irradiation into the ligand field band the reaction with CO proceeds efficiently. In all cases the same end product is obtained.

An aqueous solution of the carbonyl complex exhibits an absorption spectrum with a ligand field band at 307 nm (ϵ = 251 M^{-1} cm^{-1}) and a charge-transfer band at 205 nm (ϵ = 25 000 M^{-1} cm^{-1}). The position of the ligand field band at 307 nm (310 nm in CH_2Cl_2) is in accordance with the somewhat higher ligand field strength of the CO ligand in comparison with the CN ligand. For the sake of comparison $(n\text{-}Bu_4N)_3[Co(CN)_6]$ has its first ligand field band at 311 nm in aqueous solution (320 nm in CH_2Cl_2).

The IR spectrum of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in a KBr pellet (Figure 2) shows a broad band at 2108 cm^{-1}, which we ascribe to the stretching of the ^{12}CO ligand. This band is accompanied by a much smaller band at 2061 cm^{-1}, which should be due to the ^{13}CO stretching. Generally this ^{13}CO band is found some 45 cm^{-1} below the ^{12}CO band.[8] In the

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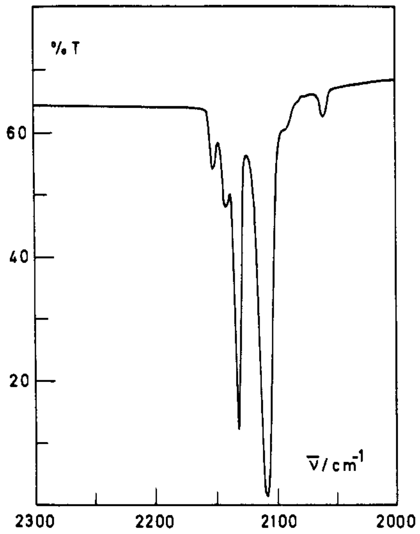

Figure 2. Infrared spectrum of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in the CO stretching region.

cyanide stretching region three well-resolved bands are found at 2152, 2142, and 2132 cm^{-1}.

The $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ complex exhibits a rather unusual behavior in aqueous solution as compared to that of other acidopentacyanocobaltate(III) complexes. The thermal stability of the new compound is strongly dependent upon the pH of the solution. At low pH (0.1 M $HClO_4$) the complex is stable, whereas in alkaline solution a fast reaction takes place, in which CN^- is released. This primary reaction is followed by a series of slower thermal reactions. The unraveling of this complex sequence is currently under investigation.

Upon irradiation of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in acid solution (0.1 M $HClO_4$) with 313-nm light the photoaquation of the CO ligand occurs:

$$Co(CN)_5CO^{2-} + H_2O \xrightarrow{h\nu} Co(CN)_5OH_2^{2-} + CO$$

During the photolysis the absorption spectra evolve over isosbestic points and after completion of the photosubstitution reaction the spectrum of the resulting product corresponds to that of the $Co(CN)_5OH_2^{2-}$ ion. The quantitative elimination of carbon monoxide in acid solution was confirmed by measuring the loss of activity of a ^{14}CO-labeled sample of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$. When the photolysis is performed in methanol as solvent, a similar photolysis occurs, leading to $Co(CN)_5(OHCH_3)^{2-}$ and CO as the sole products. The substitution of the CO ligand is accompanied by the disappearance of the band at 2108 cm^{-1} in the IR spectrum, which confirms our previous assignation of this band to the CO stretching of the $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ complex.

Registry No. $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$, 89959-52-4; $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$, 86019-13-8; $(n\text{-}Bu_4N)_2[Co(CN)_5py]$, 89959-53-5; $Co(CN)_5OH_2^{2-}$, 14842-83-2; $Co(CN)_5(OHCH_3)^{2-}$, 89959-54-6; $(n\text{-}Bu_4N)_3[Co(CN)_5N_3]$, 33848-07-6.

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