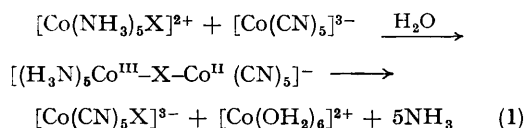


The Use of the Cyanide Ion as an Electron Mediator in an Activated Bridge Electron-transfer Reaction

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ALTHOUGH a considerable number of ligands have been used¹⁻³ as the bridging ligands, X, in reaction 1,



the cyanide ion has not been included, since, until recently,^{4,5} the oxidant $[\text{Co}(\text{NH}_3)_5\text{CN}]^{2+}$ had not been prepared.

Haim and Wilmarth⁶ used the cyanide ion as an electron mediator by employing $[\text{Fe}(\text{CN})_6]^{3-}$ as the oxidant in reaction 1, resulting in the formation of the binuclear ion $[(\text{NC})_5\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III}}(\text{CN})_5]^{6-}$. There has been no report of a case in which the

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³ J. L. Burmeister, *Inorg. Chem.*, 1964, **3**, 919.

⁴ H. Siebert, *Z. anorg. Chem.*, 1964, **327**, 63.

⁵ M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, 1964, **3**, 1573.

⁶ A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

cyanide ion acts as an electron mediator in an oxidation-reduction reaction proceeding *via* the activated bridge electron-transfer mechanism and is then transferred to the co-ordination sphere of the oxidized reductant. We now report such a case.

To a solution of potassium cyanide (0.59 g., 9 mmoles) in water (3 ml.) was added $[\text{Co}(\text{NH}_3)_5\text{CN}]\text{SO}_4$ (0.048 g., 1.8 mmoles), prepared according to the method of Siebert.² No noticeable evolution of ammonia occurred until a crystal of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ was added, whereupon the $[\text{Co}(\text{NH}_3)_5\text{CN}]\text{SO}_4$ immediately dissolved, with evolution of ammonia. The sulphate ion was precipitated as barium salt by the addition of a stoichiometric amount of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, and removed by filtration through a fritted-glass filter, the filtrate passing directly into ethanol (15 ml.) at 0°. The addition of ethanol (15 ml.) at 0° to the yellow solution resulted in the precipitation of an off-white solid which was isolated by filtration, washed with ethanol and ether, and dried *in vacuo* (CaCl_2). The yield was 0.42 g. (70% of theory).

Support for the formulation of the product as $\text{K}_3[\text{Co}(\text{CN})_6]$ was found in the microanalytical results and the infrared spectrum of the complex (Nujol mull), which was identical to that of $\text{K}_3[\text{Co}(\text{CN})_6]$ prepared according to Schlessinger's method.⁷ Both spectra, however, differed from that reported⁸ for the complex. In addition to the

reported C-N stretching frequencies of 2143, 2129, and 2126 cm^{-1} , weak bands at 2106 and 2089 cm^{-1} were found, under high resolution.

Formulation of the bridged intermediate or activated complex as $[(\text{H}_3\text{N})_5\text{Co}^{\text{III}}\text{-CN-Co}^{\text{II}}(\text{CN})_5]^-$ leads to the intriguing possibility that the initial product of the reaction is the linkage-isomeric form $[\text{Co}(\text{CN})_5\text{NC}]^{3-}$. However, if such an isomer is initially formed, its rearrangement, possibly catalyzed by $[\text{Co}(\text{CN})_5]^{3-}$ in a sequence similar to reaction 1, is so rapid as to prevent its isolation, even when the reaction was carried out in acetone at the temperature of solid carbon dioxide-acetone. The significance of this work does not lie in the synthesis of the well-known $\text{K}_3[\text{Co}(\text{CN})_6]$, but rather in the means whereby it was accomplished.

Preliminary results of tracer experiments using ^{14}C -labelled cyanide in the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ oxidant and an excess (over the ratio $[\text{CN}^-]/[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}] = 5$) of unlabelled cyanide in solution indicate^{2,4} that the reaction is indeed proceeding predominantly *via* the inner-sphere activated-bridge mechanism discussed above. An outer-sphere electron-transfer reaction² between $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and $\text{Co}(\text{CN})_6^{4-}$ (presumed³ to co-exist in equilibrium with $\text{Co}(\text{CN})_6^{3-}$ and cyanide) would, in this case, yield the same product, $\text{Co}(\text{CN})_6^{3-}$, albeit containing no radioactive cyanide.

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⁷ G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N.Y., 1962, p. 84.

⁸ K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," John Wiley and Sons, Inc., New York, N.Y., 1963, p. 166, and references contained therein.