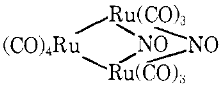
$Ru_3(CO)_{12}$ with nitric oxide. In an early paper, Manchot[4] had reported several products from the reaction of solid $Ru_3(CO)_{12}$ with NO, including one formulated as $Ru(NO)_5$.[5] Candlin[6] later reported that reaction of "moist NO" with $Ru_3(CO)_{12}$ in boiling CH_2Cl_2 gave a brown polymer whose elemental analyses were consistent with the formula $[Ru(CO)_2(NO_2)_2]_x$ and which had infrared absorption maxima at 2120, 2090, 2050, 1910, 1270, 1170, and 840 cm^{-1}. Our hope was that conditions could be found under which the cluster $Ru_4(CO)_8(NO)_4$, isoelectronic with $Rh_4(CO)_{12}$, would be formed.

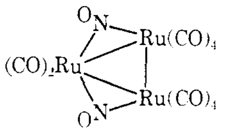
In preliminary experiments we found that the products of reaction between $Ru_3(CO)_{12}$ and NO depended strongly upon the purity of the nitric oxide. For example, nitrogen dioxide, which is present in commercial NO and which is rapidly generated by reaction of NO with air, reacted almost instantaneously with $Ru_3(CO)_{12}$ in benzene at 25° giving an insoluble yellow substance of approximate empirical composition $[Ru(CO)_3(NO_2)]_x$ (*Anal.* Calcd for RuC_3NO_5: C, 15.59; N, 6.06; H, 0.0. Found: C, 16.08; N, 6.08; H, 0.3), having infrared absorption bands (KBr pellet) at 2122 (s), 2050 (vs, broad), 2005 (m), 1490 (m, broad), 1380 (vs), 1320 (m), 1270 (m), 1180 (w, broad), 830 (m), and 814 (m) cm^{-1}. Many of these bands are present in the spectrum of Candlin's brown polymer.[6] Nitric oxide freed from NO_2 and H_2O by successive passage through 4 *N* NaOH and silica gel did not react with $Ru_3(CO)_{12}$ in benzene at 25° or in boiling CH_2Cl_2. In boiling benzene, however, passage of NO through the solution for a few minutes led to deposition of an insoluble brown polymer and the production of greenish brown solution. These solutions were flushed with N_2, cooled to 25°, filtered, and then concentrated under vacuum. Addition of *n*-hexane led to slow formation of dark green needles of the new nitrosyl carbonyl cluster $Ru_3(CO)_{10}(NO)_2$, obtained in 30–40% yield. *Anal.* Calcd for $Ru_3C_{10}N_2O_{12}$: C, 18.67; N, 4.35; H, 0.0; mol wt, 643. Found: C, 18.87; N, 4.26; H, 0.0. Replacement of benzene by cyclohexane gave similar results, but only a very slow reaction was observed in boiling chloroform, and in boiling *n*-heptane the brown polymer was the principal product. In the last case, the brown polymer contained about a 1:1 ratio of carbon to nitrogen. Under similar conditions the trisubstituted complex $Ru_3(CO)_9(PPh_3)_3$ was relatively unreactive toward NO.

The formulation of the green cluster as $Ru_3(CO)_{10}(NO)_2$ has been confirmed by low-resolution mass spectroscopy. A parent ion multiplet centered at mass 643 has been observed, along with twelve other multiplets corresponding to the loss of twelve ligands to give Ru_3^+.[7] The complex contains two more electrons than $Ru_3(CO)_{12}$ and cannot be regarded as a simple substitution product of that cluster.

The infrared spectrum of $Ru_3(CO)_{10}(NO)_2$ in cyclohexane has ν_{CO} 2110 (w), 2077 (s), 2068 (s), 2061 (sh), 2038 (s), 2030 (s), 2026 (sh), 2015 (w), and 2000 (m) cm^{-1} and ν_{NO} 1524 (w) and 1508 (m) cm^{-1}. The large number of carbonyl bands implies a low molecular symmetry, while the low ν_{NO} suggests[8] that the nitrosyls are bridging. The proposed structures **1a** and **1b** are both consistent with the analysis and spectroscopic data.



1a



1b

Complex **1** is indicated by magnetic susceptibility measurements to be diamagnetic. It is moderately air stable and slightly soluble in most organic solvents. It is unstable above 70° in solution under N_2, giving dark brown decomposition products. Two catalytic reactions of **1** have been investigated. Complex **1** reacts with dimethylacetylenedicarboxylate and the trimer hexakis(carbomethoxy)benzene was detected by vpc analysis. Stirring of a solution of 5 mg (8 μmoles) of **1** and 0.50 ml (0.34 g; 3950 μmoles) of 1-hexene in 3 ml of benzene for 22 hr under 56 psi of hydrogen led to extensive isomerization of the hexene and a small amount of hydrogenation to *n*-hexane. Although evaporation of the solvent under vacuum produced the cluster **1** unchanged, a parallel experiment without hydrogen produced no isomerization.

Other catalytic reactions of **1** and the results of an X-ray crystallographic study and of attempts to prepare other nitrosyl-substituted metal carbonyl clusters will be reported at a later time.

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[4] W. Manchot and W. J. Manchot, *Z. Anorg. Allg. Chem.*, **226**, 385 (1936).

[5] Manchot's analytical data actually agree somewhat better with the formulation $Ru(NO)_2(NO_2)_2$ which is probably more reasonable.

[6] J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. Ind.* (London), 1960 (1966).

[7] The multiplets are due to the complex isotopic distribution of the triruthenium unit. Computer analysis of the entire spectrum is in progress.

[8] For example, in di-μ-nitrosyl-bis(nitrosyl-π-cyclopentadienylchromium) the terminal nitrosyl frequency is 1672 cm^{-1} while that of the bridging nitrosyls is 1505 cm^{-1}; *cf.* R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964), and R. B. King, *ibid.*, **6**, 30 (1967), for this and other examples.

[9] National Science Foundation Predoctoral Fellow 1967–present.

[10] On leave from Princeton University Feb–Aug 1969.

[11] (a) Author to whom inquiries should be addressed. (b) This work was supported by National Science Foundation Grant No. GP 9101 and the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

Pulse Radiolysis of Aqueous Solutions of Cobalt Cyanide Complexes. The Detection of Pentacyanocobaltate(I) and Other Transients

Sir:

We report here some results of pulse radiolysis experiments on aqueous solutions of cobalt cyanide complexes, including the direct detection of several important transient species, among them pentacyanocobaltate(I). Although the latter species has been postulated as a reaction intermediate[1,2] and has been the subject of considerable interest and speculation, it does not appear to have previously been directly observed.

Hydrated electrons (e_{aq}^-) were generated in deaerated solutions containing various cobalt cyanide complexes, using 0.4-μsec pulses of 15-MeV electrons from Ar-

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[1] J. Hanzlik and A. A. Vlček, *Inorg. Chem.*, **8**, 669 (1969).

[2] J. Hanzlik and A. A. Vlček, *Chem. Commun.*, 47 (1969).

gonne National Laboratory's ARCO linear accelerator, in accord with the general procedures described elsewhere.[3] Experimental conditions were maintained so as to ensure the rapid ($t_{1/2} \sim 0.1$ µsec) scavenging of OH radicals, either by methanol ($\sim 10^{-2}$ *M*) in the case of the $Co(CN)_5{}^{3-}$ solutions, or by H_2 (~ 0.1 *M*, achieved by using a high-pressure cell[4] containing 100 atm of H_2) in the case of the other solutions. The pH, in each case, was maintained at 13; under these conditions H atoms were rapidly ($t_{1/2} \sim 0.35$ µsec) converted by OH^- to $e_{aq}{}^-$ so that, for our purposes, $e_{aq}{}^-$ was effectively the only reactive species generated by the pulse radiolysis. The reactions of the hydrated electrons with the cobalt complexes were monitored spectrophotometrically as previously described,[3] the spectra of transient species being deduced from the absorbance changes accompanying their formation and/or decay. The overall stoichiometries of the reactions were confirmed in steady-state irradiation experiments using a ^{60}Co γ source.

Pulse radiolysis experiments on aqueous solutions of $Co(CN)_5{}^{3-}$ ($\sim 10^{-5}$ *M*), in which the generation and decay of $e_{aq}{}^-$ were followed at 578 nm (ϵ 1.1×10^4 M^{-1} cm^{-1}), revealed a reaction between $e_{aq}{}^-$ and $Co(CN)_5{}^{3-}$ which obeyed the second-order rate law, $k_1 \cdot [e_{aq}{}^-][Co(CN)_5{}^{3-}]$, with $k_1 = (1.4 \pm 0.1) \times 10^{10}$ M^{-1} sec^{-1}. The initial product of this reaction is a transient, identified below as pentacyanocobaltate(I) (λ_{max} 280 nm, $\epsilon_{max} \sim 8 \times 10^3$), which undergoes first-order decay ($k_2 = (1.0 \pm 0.1) \times 10^5$ sec^{-1}) to yield $Co(CN)_5H^{3-}$. In D_2O solutions the value of k_1 was substantially the same as in H_2O, whereas the value of k_2 was reduced to 1.6×10^4 sec^{-1}, one-sixth its value in H_2O. We interpret these observations in terms of the following reaction sequence.

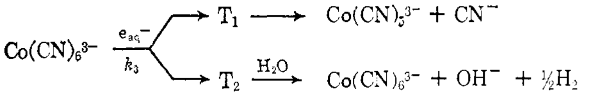
$$Co(CN)_5{}^{3-} + e_{aq}{}^- \xrightarrow{k_1} Co(CN)_5{}^{4-} \qquad (1)$$

$$\underline{Co(CN)_5{}^{4-} + H_2O \xrightarrow{k_2} Co(CN)_5H^{3-} + OH^- \qquad (2)}$$

$$Co(CN)_5{}^{3-} + H_2O + e_{aq}{}^- \longrightarrow Co(CN)_5H^{3-} + OH^-$$

Pentacyanocobaltate(I), $Co(CN)_5{}^{4-}$, has previously been proposed as an intermediate in the electrochemical oxidation of $Co(CN)_5H^{3-}$,[2] in the electrochemical reduction of $Co(CN)_5{}^{3-}$,[5] and in the base-catalyzed oxidation of $Co(CN)_5H^{3-}$ by $Co(CN)_5I^{3-}$ [6] and by benzoquinone.[1]

Pulse radiolysis experiments were also performed on aqueous solutions of various cobalt(III) cyanide complexes, including $Co(CN)_6{}^{3-}$, $Co(CN)_5OH^{3-}$, and $Co(CN)_5I^{3-}$, in the hope of generating and characterizing the corresponding unstable transient six-coordinate cobalt(II) species, $Co^{II}(CN)_6{}^{4-}$, $Co^{II}(CN)_5OH^{4-}$, etc. These experiments yielded somewhat more complicated results, the significance of which is not yet fully established. For example, electron capture by $Co(CN)_6{}^{3-}$ ($\sim 10^{-4}$ *M*) occurred with a second-order rate constant, $k_3 = (5.0 \pm 0.5) \times 10^9$ M^{-1} sec^{-1}, corresponding to complete electron capture with $t_{1/2} \sim 1.5$ µsec. The initially observed products following electron capture were two distinct transients, T_1 (λ_{max} 280 nm, ϵ 7×10^3; λ_{max} 965 nm, $\epsilon \sim 5 \times 10^2$) and T_2 (λ_{max} 270–275 nm, $\epsilon \sim 10^3$), which decayed with half-lives of $\sim 10^{-8}$ and 10^{-5} sec, respectively, in accord with the pattern depicted by eq 3 and 4, to yield $Co(CN)_5{}^{3-}$ ($\sim 50\%$) and $Co(CN)_6{}^{3-}$ ($\sim 50\%$), respectively.



$$Co(CN)_6{}^{3-} \xrightarrow[k_3]{e_{aq}{}^-} T_1 \longrightarrow Co(CN)_5{}^{3-} + CN^- \qquad (3)$$

$$Co(CN)_6{}^{3-} \xrightarrow[k_3]{e_{aq}{}^-} T_2 \xrightarrow{H_2O} Co(CN)_6{}^{3-} + OH^- + \tfrac{1}{2}H_2 \qquad (4)$$

While the available information does not provide an entirely convincing basis for the identification of T_1 and T_2, plausible suggestions are that T_2 corresponds to $Co^{II}(CN)_6{}^{4-}$ [7] (with properties perhaps best described as those of an "electron-adduct" of $Co(CN)_6{}^{3-}$),[9] whereas T_1 (whose spectrum resembles that of $Co(CN)_5{}^{3-}$) might be a linkage isomer of $Co(CN)_5{}^{3-}$, such as $Co(CN)_4NC^{3-}$. The latter could arise through the rapid dissociation of a precursor such as $Co(CN)_4(NC)_2{}^{4-}$, which has been proposed as one of the products of electron irradiation of solid $K_3Co(CN)_6$.[10]

Qualitatively similar results (in each case corresponding to two transients, one of which reverts to the parent compound and the other, which decays to $Co(CN)_5{}^{3-}$) were also obtained in pulse radiolysis experiments on aqueous solutions of other cobalt(III) cyanide complexes including $Co(CN)_5OH^{3-}$, $Co(CN)_5I^{3-}$, and $Co(CN)_5NCS^{3-}$ [11,12]

Acknowledgments. Based on work performed under the auspices of the U. S. Atomic Energy Commission. The award of an Argonne Universities Association–Argonne National Laboratory fellowship to one of us (G. D. V.) is gratefully acknowledged.

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(3) A. S. Ghosh-Mazumdar and E. J. Hart, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 193, and references cited therein.

(4) E. M. Fielden and E. J. Hart, *Radiat. Res.*, 33, 426 (1968).

(5) A. A. Vlček, *Pure Appl. Chem.*, 10, 61 (1961).

(6) J. Halpern and M. Pribanić, unpublished data.

(7) An intermediate of this composition has previously been postulated[8] in the "outer-sphere" oxidation of $Co(CN)_5{}^{3-}$ to $Co(CN)_6{}^{3-}$, by $Co(NH_3)_6{}^{3+}$ and other cobalt(III) complexes.

(8) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

(9) An analogous transient, $Au(CN)_2{}^{2-}$, also exhibiting properties of an "electron-adduct," has been observed[3] in pulse radiolysis experiments on $Au(CN)_2{}^-$ solutions. Such "electron-adducts" appear to be distinctively characteristic of cyanide complexes.

(10) J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Struct.*, 1, 127 (1967).

(11) We are grateful to Professor H. B. Gray, D. Gutterman, and G. Rossman of the California Institute of Technology for samples of these compounds and for valuable discussions.

(12) Preliminary pulse radiolysis experiments on aqueous solutions of $Mo(CN)_8{}^{4-}$ yielded analogous results.[11] Electron capture by $Mo(CN)_8{}^{4-}$ occurs with a rate constant of 7.1×10^9 $M^{-1}sec^{-1}$, yielding two transients, one of which decays with a rate constant of 1.3×10^2 sec^{-1} to $Mo(CN)_7{}^{4-}$ + CN^- ($\sim 60\%$), and the second with a rate constant of 2×10^4 sec^{-1}, presumably reverting to $Mo(CN)_8{}^{4-}$.

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The Stereochemical Course of Deamination of Acyclic Secondary Carbinamines in Water. The Role of Micelles[1]

Sir:

Carbinol formation *via* aqueous HNO_2 deamination of acyclic secondary carbinamines is reported to involve

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(1) Presented at the 158th National Meeting of the American Chemical Society, Sept 8, 1969, New York, N. Y.