With triphenylarsine sufficient Pd–S π bonding is possible to make the S– isomer also preparable. Tributylarsine, which should be a slightly weaker π acceptor than triphenylarsine, gives only the S– isomer in the solid state, though on fusion the N– isomer also forms.

In the series of compounds where the donor atom is an aromatic nitrogen atom, 5-nitro-*o*-phenanthroline gives the N– isomer whereas pyridine and *o*-phenanthroline give the S– isomer. Intermediate between these two is the ligand dipyridyl which gives both linkage isomers.

Experimental

The compounds were prepared by the procedure of Burmeister and Basolo[5] and analyzed satisfactorily for nitrogen. The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer Model 337 spectrophotometer.

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The Standard Oxidation Potentials of the Silver–Silver Cobalticyanide and Mercury–Mercurous Cobalticyanide Electrodes at 25°

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There are few thermodynamic data available on cobalticyanide salts.[1-3] The solubility product of $Ag_3Co(CN)_6$ obtained from potentiometric titration data[1] of a cell with liquid junctions is too large to be consistent with the chemical behavior of this salt. It has been found in this investigation that the solubility product for $Ag_3Co(CN)_6(s)$ obtained from cells free from liquid junctions is much smaller than the previously reported value.

Experimental

Reagents.—J. T. Baker reagent grade KCl was used without further purification. The $K_3Co(CN)_6$ was obtained from G. F. Smith Chemical Co. The impure salt was recrystallized four times from distilled water, the hot (60°) concentrated solution being filtered each time. The mercury (triple distilled, purity exceeds A.C.S. specifications) was obtained from Bethlehem Apparatus Co. Samples of $Ag_3Co(CN)_6$ and $(Hg_2)_3[Co(CN)_6]_2 \cdot 4H_2O$ were obtained by adding slowly with continuous stirring a 0.1 *M* solution of $K_3Co(CN)_6$ to a hot (50–60°) acidified 0.1 *M* solution of reagent grade $AgNO_3$ and $Hg_2(NO_3)_2$ (in 10% excess), respectively. The precipitates were washed by repeated decantation with distilled water until tests for metal ions proved negative and then air-dried in the dark.

Anal.[4] Calcd. for $Ag_3Co(CN)_6$: C, 13.37; N, 15.60. Found: C, 13.45; N, 15.57. Calcd. for $(Hg_2)_3[Co(CN)_6]_2 \cdot 4H_2O$: C, 8.45; H, 0.47; N, 9.85. Found: C, 8.44; H, 0.40; N, 9.85. Calcd. for $K_3Co(CN)_6$: C, 21.68; N, 25.29. Found: C, 21.52; N, 25.35.

Electrical Cell Measurements.—Voltages were measured with a Leeds and Northrup Type K-3 certified potentiometer and a Leeds and Northrup No. 2430C galvanometer. The voltage standard was an Eppley Laboratory unsaturated Weston cell (certified June 1964). Electrode compartments were similar to those described by Hills and Ives,[5] and the calomel electrodes were set up according to their prescription. The insides of the electrode compartments were silicone-coated.[5] The cell leads were brought in through a capillary to the base of the compartment and sealed in place with paraffin wax. These leads were of platinum and were completely covered with mercury. The silver electrode was a piece of Englehard Industries No. 24 B. and S. gauge silver wire bent in a loop so that the end was beneath the wax surface. This silver loop was electroplated in place by rapid electrolysis of a silver nitrate solution. A new silver electrode was prepared for each cell measurement. Air was excluded from all cells by a stream of purified nitrogen from a presaturator filled with cell electrolyte. Light was excluded from the silver–silver cobalticyanide and mercury–mercurous cobalticyanide electrodes by wrapping the electrode compartments in aluminum foil. The solid phases in these electrodes were white at the completion of the measurements. The cells were kept at 25.0 ± 0.005° in a grounded water bath. The amalgam junction connector used has been described.[6] The dilute (0.01 wt. % K) potassium amalgam was prepared by electrolysis of 2 *M* KOH with a mercury cathode and dried on the vacuum line.

Results

Mercurous Cobalticyanide.—The potential of the mercury-mercurous cobalticyanide electrode was determined in the cell

$$\mathrm{Hg(l)|Hg_2Cl_2(s)|KCl(aq)|\underset{0.01\%}{K(Hg)}|K_3Co(CN)_6(aq)|(Hg_2)_3[Co(CN)_6]_2(s)|Hg(l)}$$

Because of a side reaction between the K(Hg) and the $K_3Co(CN)_6$ solution (color changes from very pale to deep yellow in the vicinity of the K(Hg) the cell was allowed to equilibrate overnight with pure mercury in the connector. The mercury was then displaced with 0.01% K(Hg) and stable voltages could be obtained for 2–3 hr. if the $K_3Co(CN)_6$ in contact with the K(Hg) was occasionally renewed. If left to stand overnight in contact with K(Hg) the $K_3Co(CN)_6$ solution became a deep yellow in color and the mercurous cobalticyanide solid phase was no longer present.

At 0.125 *m* KCl and 0.128 *m* $K_3Co(CN)_6$ the observed cell voltage was (calomel negative) 117 ± 0.5 mv., and at 0.150 *m* KCl and 0.0500 *m* $K_3Co(CN)_6$ it was 159 ± 0.5 mv. Application of the Nernst equation to the cell reaction yields at 25° $(Hg_2)_3[Co(CN)_6]_2(s) + 6KCl(aq) = 3Hg_2Cl_2(s) + 2K_3Co(CN)_6(aq)$, $E = E_1° - E_2° - 0.07888 \log 27^{1/4} m\gamma_{\pm} + 0.11832 \log m'\gamma_{\pm}'$. $E_1°$ is the standard oxidation potential of the

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[1] C. Drăgulescu and P. Tribunescu, *Studii Certari, sti. chim.*, **6**, 59 (1959); *Chem. Abstr.*, **54**, 24066*b* (1960).

[2] L. G. Hepler, J. R. Sweet, and R. A. Jesser, *J. Am. Chem. Soc.*, **82**, 304 (1960).

[3] R. A. Wynveen, J. L. Dye, and C. H. Brubaker, Jr., *ibid.*, **82**, 4441 (1960).

[4] Analyses carried out by the Microanalytical Laboratory of the University of California, Berkeley, Calif.

[5] G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 311 (1951).

[6] P. A. Rock and R. E. Powell, *Inorg. Chem.*, **3**, 1593 (1964).

calomel electrode (−0.2680 v.),[5] $E_2°$ is the standard oxidation potential of the mercury–mercurous cobalticyanide electrode, $m\gamma_\pm$ refers to $K_3Co(CN)_6$(aq), and $m'\gamma_\pm'$ refers to KCl(aq). From the observed cell voltages, the above stated molalities, and the mean molal activity coefficients of $K_3Co(CN)_6$[3] and KCl,[7] the standard oxidation potential of the mercury–mercurous cobalticyanide electrode is calculated to be

$$6Hg(l) + 2Co(CN)_6^{3-}(aq,\ a = 1) = (Hg_2)_3[Co(CN)_6]_2(s) + 6e^- \quad E° = -0.427 \pm 0.001 \text{ v.}$$

In the calculation of this $E°$ the solid phase was assumed to be anhydrous salt, although it is probably the tetrahydrate. This introduces no significant uncertainty in $E°$, however, since the correction for the activity of water is within the experimental error.

Silver Cobalticyanide.—The potential of the silver–silver cobalticyanide electrode was determined in the cell

$$Ag(s)|Ag_3Co(CN)_6(s)|K_3Co(CN)_6(aq)|(Hg_2)_3[Co(CN)_6]_2(s)|Hg(l)$$

If the solid phases controlling the activities of Ag^+ and Hg_2^{2+} ions in solution are those represented in the cell diagram the observed cell voltage should be independent of the $K_3Co(CN)_6$ concentration and $E = E°$. For $K_3Co(CN)_6$ molalities of 0.10, 0.20, and 0.50 the observed cell voltages were (silver negative): 0.130 ± 0.001, 0.128 ± 0.001, and 0.129 ± 0.001 v., respectively. This cell came to equilibrium in about 1 day and had a constant voltage for as long as it was followed (6–8 days in each case). The observed cell voltage was unaffected by the agitation of the electrode components.

Using the above-determined value of the mercury–mercurous cobalticyanide standard oxidation potential, the standard oxidation potential of the silver–silver cobalticyanide electrode is computed to be

$$3Ag(s) + Co(CN)_6^{3-}(aq,\ a = 1) = Ag_3Co(CN)_6(s) + 3e^- \quad E° = -0.298 \pm 0.001 \text{ v.}$$

Discussion

Taking the standard oxidation potential at 25° of the Ag–Ag^+ electrode as −0.799 v. and that of the Hg–Hg_2^{2+} electrode as −0.789 v.,[8] one computes

$$3Ag^+ + Co(CN)_6^{3-} = Ag_3Co(CN)_6(s) \quad \Delta G° = -34.66 \text{ kcal.}$$

$$3Hg_2^{2+} + 2Co(CN)_6^{3-} = (Hg_2)_3[Co(CN)_6]_2(s) \quad \Delta G° = -50.09 \text{ kcal.}$$

From these $\Delta G°$ values the solubility products of $Ag_3Co(CN)_6$ and $(Hg_2)_3[Co(CN)_6]_2(s)$ are computed to be 3.9×10^{-26} and 1.9×10^{-37}, respectively.

The previously reported value[1] for K_{sp} of $Ag_3Co(CN)_6$ is 8.6×10^{-21}. This value was obtained from potentiometric titration data in cells using salt bridges, a method which can introduce large uncertainties in the data. The K_{sp} values differ, however, by more than can be accounted for by a liquid junction potential of even 0.05 v., and the K_{sp} obtained in the potentiometric investigation may have been adversely affected by failure to attain equilibrium as well, since it was found in this investigation that the silver–silver cobalticyanide electrode is slow to come to equilibrium.

Contribution from the Jet Propulsion Laboratory,
California Institute of Technology,
Pasadena, California

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(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, New York, N. Y., 1959.

(8) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

Chloride Alkoxides of Pentavalent Tungsten[1]

By Olgierd J. Klejnot[2]

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Studies aimed at syntheses of the unknown tungsten hexa- and pentaalkoxides have led to the first isolation of tungsten(V) chloride alkoxides (I–III). The reported green $W_2Cl_4(OC_2H_5)_6$[3] obtained by reducing pentavalent solutions seems to be tetravalent with two ethanol ligands in place of two ethoxo ligands.

Dissolution of tungsten hexachloride in alcohols gave long-known yellow solutions,[3] but the evolution of chlorine in methanol or ethanol has only been noted now

$$WCl_6 + 2C_2H_5OH \longrightarrow {}^1/_2Cl_2 + WCl_3(OC_2H_5)_2 + 2HCl \quad (1)$$

$$Cl_2 + C_2H_5OH \longrightarrow CH_3CHO + 2HCl \quad (2)$$

A violent reaction, which probably involves the aldehyde, occurs at high concentration of products. On evaporation the reaction solutions render paramagnetic, ink-blue trichloride dialkoxides, $WCl_3(OCH_3)_2$ (I) and $WCl_3(OC_2H_5)_2$ (II), whose blue solutions in alcohol give with hydrogen chloride a pale yellow color, reverting to blue on partial evaporation *in vacuo*. The trichloride dialkoxides react with moisture and oxygen. In alcohol they form soluble complexes with NaF, NaCl, and the methoxides of Li, Na, and K. Pure alcohol solutions, however, show at room temperature a slow limited solvolysis, up to a low concentration of HCl, with blue (methanol) or red (ethanol) color. From a solution of II, di-μ-chloro-dichlorohexaethoxoditungsten(V) (III) is slowly precipitated in 4–15% yield

$$2WCl_3(OC_2H_5)_2 + 2C_2H_5OH \longrightarrow W_2Cl_4(OC_2H_5)_6 + 2HCl \quad (3)$$

Diamagnetic, red dimer III is inert to water, acids, and oxidizing agents, but is reactive toward bases. The dimeric formula and chemical evidence suggest a bioctahedral structure with two bridging chloro ligands and pentavalent tungsten atoms. The compound is

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[1] Results of one phase of research supported by the National Aeronautics and Space Administration under Contract No. NAS7-100.

[2] Unified Science Associates, Inc., Pasadena, Calif. 91105.

[3] A. Fischer and L. Michiels, *Z. anorg. Chem.*, **81**, 102 (1913); A. Fischer, *ibid.*, **81**, 170 (1913).