um(IV) and 0.4 $M$ phenol was mixed with 0.01 and 0.3 $M$ solutions of chlorine(III) in a Durrum–Gibson stopped-flow apparatus and the absorbance was monitored at 360 nm. At this wavelength chlorine dioxide exhibits an absorbance maximum with a molar absorptivity of 1250 $M^{-1}$ cm$^{-1}$.

The maximum absorbance change observed for the 0.01 and 0.30 $M$ chlorine(III) solutions is 0.040 and 0.200 absorbance unit, respectively. This increase in absorbance can be attributed either to the formation of chlorine dioxide or to the $UO_2^{2+}$–$ClO_2^-$ complex.[52] If the absorbance increase is due entirely to chlorine dioxide, the effective decrease in chlorine(III) concentration would once again be less than 1%. Gordon and Kern[52] observed the formation of a charge-transfer complex between $UO_2^{2+}$ and chlorite ion. The formation constant for the charge-transfer complex was assigned an approximate value of 0.02 $M^{-1}$. The molar absorptivity of this complex is estimated as $5 \times 10^6$ $M^{-1}$ cm$^{-1}$ at 360 nm. Since the uranium(IV) solution contained $\sim 10^{-3}$ $M$ uranium(VI), the maximum concentration of the complex, assuming that the 0.20 absorbance unit change is due entirely to the complex, is calculated as $2 \times 10^{-8}$ $M$. Based on this, the amount of chlorine(III) complexed is only $1 \times 10^{-8}$ $M$.

It is obvious from these calculations that the effective decrease in chlorine(III) concentration would be less than 1% and nowhere near the required 30%. Therefore, the observed decrease in the rate cannot be attributed to a reduction in the effective chlorine(III) concentration by these pathways.

The observed absorbance change at 360 nm, attributed to the production of chlorine dioxide and/or the formation of a uranium(VI)–chlorite ion complex, does not preclude the possibility that the increase in absorbance is due to the formation of a uranium(IV)–chlorous acid complex.

A preference for a two-electron oxygen atom transfer in the reaction of uranium(IV) and oxygen-containing oxidizing agents has been established by Gordon and Taube.[42] Ondrus and Gordon[12,53] suggested that the preference for a one-electron transfer, by means of an inner-sphere process, appears to be associated with direct halogen bonding rather than oxygen bonding.

The most probable difference between reactions 16 and 17 would be the way in which the oxidizing agent is bonded to the uranium(IV). The reaction proposed in eq 17 would lead to products but that in eq 16 would not.

In the present system, the tracer study indicates that the principal pathway for the uranium(IV)–chlorine(III) reaction involves a two-electron oxygen-transfer process. This requires that the oxygen atom of the chlorite ion be bonded to uranium(IV) in the activated complex. The observed oxygen-transfer result rules out the possibility of a major contribution from the one-electron process. However, if chlorous acid is bonded to uranium(IV) by means of the chlorine atom, this is not inconsistent with the formation of a nonproductive intermediate such as is suggested by eq 16. This could account for the retardation of the rate of reaction by chlorous acid.

The reaction reported here is in accord with the mechanisms of other reactions of metal ions which involve the halogenate oxidants; that is, the two-electron transfer process appears to be associated with direct oxygen bonding in the first coordination sphere of the reductant.

**Acknowledgments.**—The authors with to express their appreciation to T. W. Newton for helpful comments and to the Atomic Energy Commission and the National Science Foundation through the Office for International Programs for financial support.

(52) G. Gordon and D. M. H. Kern, *Inorg. Chem.*, **3**, 1055 (1964).

(53) G. Gordon, *Proc. Int. Conf. Coord. Chem.*, **13**, 11 (1970).

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# Tetraalkylammonium Pentacyanocobaltates. Their Preparation, Properties, and Reactivity

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Conductivity, spectral, electrochemical, and magnetic measurements on tetraalkylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile solution are discussed and indicate the presence of the species $(CH_3CN)_2Co(CN)_2$, $[CH_3CNCo(CN)_3]^-$, and $[Co(CN)_5]^{3-}$, in relative concentrations dependent on the $[CN^-]/[Co]$ ratio. The latter ion has been isolated as the solid complexes $(R_4N)_3[Co(CN)_5]$ (Ia, R = $C_2H_5$; Ib, R = $n$-$C_4H_9$). The reactions of compounds I are discussed in relation to those of aqueous solutions of $M_3[Co(CN)_5]$ (II, M = alkali metal), previously studied by other workers. Reaction of compounds I with oxygen gives $(R_4N)_3[Co(CN)_5O_2] \cdot 1.5H_2O$ (IIIa, R = $C_2H_5$; IIIb, R = $n$-$C_4H_9$).[2]

The pentacyanocobalt(II) ion,[3,4] $[Co(CN)_5]^{3-}$, has been much investigated in recent years because of its behavior as a homogeneous hydrogenation catalyst.[5–8] Typically, solutions containing this ion are prepared by reaction of a cobalt(II) compound with an alkali metal cyanide. As noted by Kwiatek,[6] previous studies

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(2) Because of the interest in the pentacyanocobalt(II) ion, samples of compound Ia and also of compound IIIa have been sent to Dr. J. J. Daly, Monsanto Research, S.A., Zürich, Switzerland, for determination of their crystal and molecular structures.

(3) A. W. Adamson, *J. Amer. Chem. Soc.*, **73**, 5710 (1951).

(4) B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966), specifically pp 128–142.

(5) J. E. Lyons, L. E. Rennick, and J. L. Burmeister, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 2 (1970).

(6) J. Kwiatek, *Catalysis Rev.*, **1**, 37 (1967).

(7) J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **No. 70**, 207 (1968).

(8) J. Kwiatek, I. L. Mador, and J. K. Seyler, *ibid.*, **No. 37**, 201 (1963).

have, for reasons of solubility, been carried out almost exclusively with aqueous solutions, though there are a few reports[9–15] of the use of alcohols and one of the use of acetic acid[12] as the solvent. Additionally, Gutmann and his coworkers[16–19] have reported that, by using tetraethylammonium cyanide, the pentacyanocobalt(II) ion may be obtained in a variety of aprotic solvents. The compound $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5]$ has presumably been made in aqueous solution by Venerable[20] by reaction of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ with hydrated electrons. Our object was to obtain the $[Co(CN)_5]^{3-}$ ion in organic solvents by the use of tetraalkylammonium cyanides. Initially we were unaware that Gutmann and coworkers[16–19] had previously demonstrated this point, but since they report[17] only "decomposition" in our chosen solvent, acetonitrile, there has been little duplication of results. Additionally our own work includes a more extensive characterization of the cobalt–cyanide complexes both in solution and in the solid state.

## Experimental Section

Unless otherwise stated, all work was carried out in a drybox, continuously flushed with nitrogen. Typical oxygen levels were below 10 ppm.

**Materials.**—Tetraalkylammonium cyanides were prepared by the method of Solodar.[21] Anhydrous cobalt(II) chloride was obtained from Alfa Inorganics, Beverly, Mass. "Spectroquality" acetonitrile from Matheson Coleman and Bell, Norwood, Ohio, dried over molecular sieves, was used for spectral, conductivity, electrochemical, and magnetic measurements. Dimethylformamide from Fischer Scientific Co., Fair Lawn, N. J., dried over copper(II) sulfate and, subsequently, distilled *in vacuo* was also used for electrochemical studies. Hexamethylphosphoramide was obtained from Eastman Chemical Co., Kingsport, Tenn. ("Eastman Inhibitor HPT") and was dried by dissolution of sodium until the blue color of solvated electrons persisted *in the solution;* it was then distilled *in vacuo* from sodium and stored under nitrogen.

**Conductivity Studies.**—Measurements were made with a Serfass conductivity bridge, Model RCM-15BI, and a cell with platinized platinum electrodes, of cell constant 1.00. Tetraethylammonium cyanide ($1 \times 10^{-1}$ *M*) in deoxygenated acetonitrile was added in 1.0-ml portions to a solution (100 ml) of cobalt(II) chloride ($2 \times 10^{-3}$ *M*) in the same solvent. The conductivity of the solution was measured after each addition. The combined data from two such runs are shown in Figure 1 together with a reference curve obtained as indicated.

**Electronic Spectra.**—Spectra were measured on either a Cary 14 (ultraviolet, visible, and near-infrared) or a Bausch and Lomb Spectronic 505 (ultraviolet only) instrument, the latter being used for measurement of extinction coefficients. A Teflon-plugged 1-cm cell, which was filled in the drybox, was used for the measurements. They were obtained with pure acetonitrile as reference, except for one measurement at $[CN^-]/[Co] = 300$ for which tetraethylammonium cyanide ($6 \times 10^{-2}$ *M*) in acetonitrile was used. Figures 2–4 show typical spectra. Figure 5 shows a plot of the apparent extinction coefficient of the band due to the $[Co(CN)_5]^{3-}$ ion *vs.* the $[CN^-]/[Co]$ ratio.

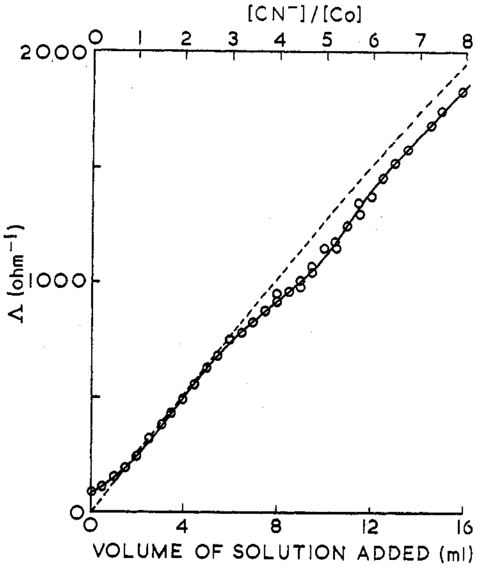

Figure 1.—Conductivity (Λ) of an acetonitrile solution of anhydrous cobalt(II) chloride ($2.0 \times 10^{-3}$ *M;* 100 ml) to which tetraethylammonium cyanide ($1.0 \times 10^{-1}$ *M*) in the same solvent is added in portions (full curve) and of acetonitrile (100 ml) to which tetraethylammonium perchlorate ($1.0 \times 10^{-1}$ *M*) in the same solvent is added in portions (broken curve). The measurements were made at room temperature (*ca.* 24°).

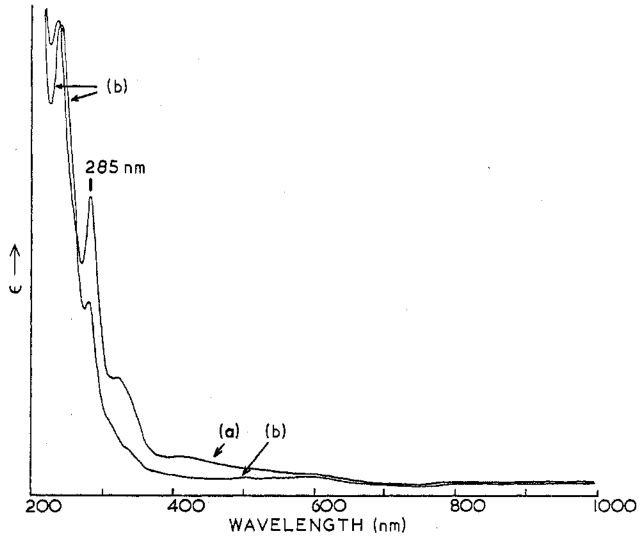

Figure 2.—Electronic spectra of tetraethylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile: $[Co] = 2.0 \times 10^{-4}$ *M;* $[CN^-]/[Co] = 5$ (a) and 4 (b).

**Electrochemical Measurements.**—Polarography was carried out with a Beckman Electroscan 30 instrument. Because of the necessary height of the mercury reservoir, these measurements could not be conveniently carried out in the drybox. Therefore, a cell which could be filled in the drybox, then made airtight, and brought out for the measurements (Figure 6) was used.

Cyclic voltammetry was carried out in the drybox using a Wenking Model 66TA1 potentiostat, an Exact Model 505 function generator, and a Tektronics 502-A dual-beam oscilloscope equipped with a Polaroid camera for permanent recording of the current–voltage curves. The working electrode was a mercury drop sitting on a mercury-coated platinum wire which had been sealed into glass and filed flush. Typical polarograms and cyclic voltammograms are shown (Figures 7 and 8).

**Magnetic Measurements.**—Magnetic moments in solution were measured on a Varian T-60 machine using a normal nmr tube with a capillary insert. The solvent was acetonitrile containing 1.5 mol % tetramethylsilane. The shift of the tetramethylsilane resonance in some cobalt–cyanide solutions (outer

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(9) F.-D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).

(10) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

(11) T. Funabiki and K. Tarama, *Bull. Chem. Soc. Jap.*, **44**, 945 (1971).

(12) G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discuss. Faraday Soc.*, **46**, 110 (1968).

(13) A. F. Mabrouk, H. J. Dutton, and J. C. Cowan, *J. Amer. Oil Chem. Soc.*, **41**, 153 (1964).

(14) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964).

(15) N. K. King and M. E. Winfield, *ibid.*, **83**, 3366 (1961).

(16) V. Gutmann and K. H. Wegleitner, *Monatsh. Chem.*, **99**, 368 (1968).

(17) V. Gutmann and O. Bohunovsky, *ibid.*, **99**, 751 (1968).

(18) V. Gutmann and A. Scherhaufer, *Inorg. Chim. Acta*, **2**, 325 (1968).

(19) A. Weisz and V. Gutmann, *Monatsh. Chem.*, **101**, 19 (1970).

(20) G. D. Venerable, *Inorg. Chem.*, **10**, 1999 (1971).

(21) A. J. Solodar, *Syn. Inorg. Metal-Org. Chem.*, **1**, 141 (1971).

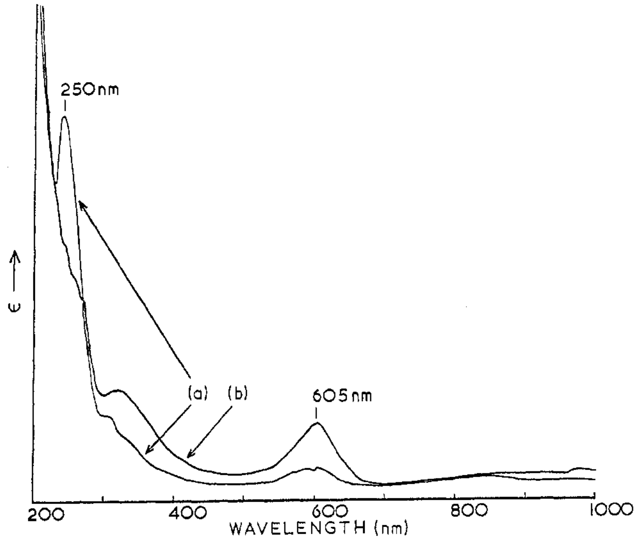

Figure 3.—Electronic spectra of tetraethylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile: [Co] = 2.0 × $10^{-4}$ *M;* [$CN^-$]/[Co = 3 (a) and 2 (b).

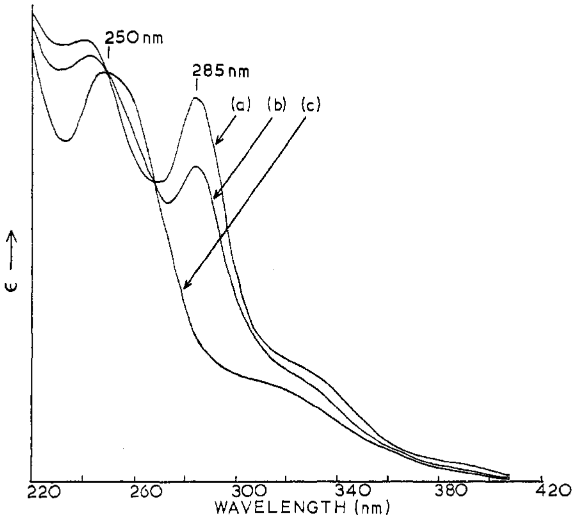

Figure 4.—Ultraviolet spectra of tetraethylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile: [Co] = 2.0 × $10^{-4}$ *M;* [$CN^-$]/[Co] = 5.5 (a), 4.5 (b), and 3.5 (c).

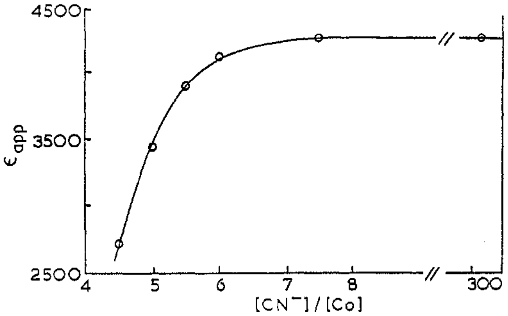

Figure 5.—Variation of apparent extinction coefficient ($\epsilon_{app}$) of the band at 285 nm due to the $[Co(CN)_5]^{3-}$ ion with [$CN^-$]/[Co] ratio, measured in acetonitrile, [Co] = 2.0 × $10^{-4}$ *M*. The flat portion of the curve gives the true extinction coefficient (4300).

tube) from that in the neat solvent (inner capillary tube) is shown in Table I along with the calculated effective magnetic moments.

A Varian V-4502 spectrometer was used for esr measurements, the samples being contained in quartz tubes of either 1 mm (solid samples) or 3 mm (solution samples) internal diameter. The tubes were filled and capped in the drybox, then removed, and sealed with a hot flame.

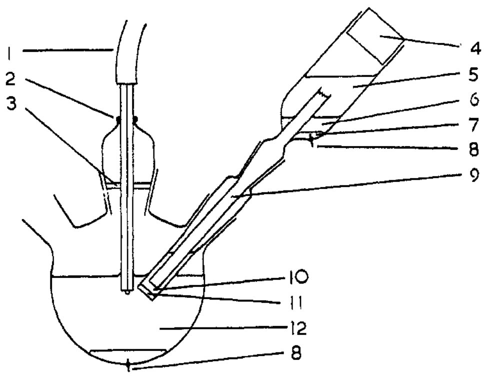

Figure 6.—Cell design for polarography: (1) flexible hose connection to mercury reservoir (the reservoir was clamped to a stand small enough that it and the cell could be taken in and out of the drybox); (2) Apiezon Q seal; (3) spacer; (4) rubber plug; (5) saturated KCl solution; (6) mixture of mercury and mercurous chloride; (7) mercury; (8) platinum wire contact; (9) Agar plug; (10) background electrolye solution; (11) glass frit; (12) background electrolyte solution and depolarizer.

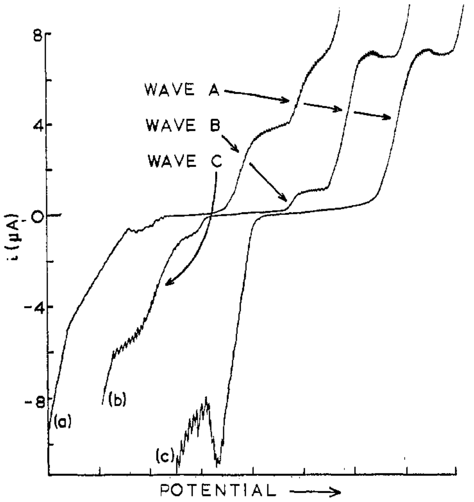

Figure 7.—Polarograms of tetraethylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile, containing tetraethylammonium perchlorate (1.0 × $10^{-1}$ *M*): [Co] = 2.0 × $10^{-3}$ *M;* [$CN^-$]/[Co] = 4(a), 5(b) and 6(c). The abscissa scale is 0.5 V/division and potentials are measured with reference to a saturated calomel electrode. Polarograms a and b start at 0.0 V. Curve c was off scale at that voltage and consequently the curve shown starts at *ca.* −0.25 V. The current (*i*) corresponding to oxidative processes is denoted by a negative sign.

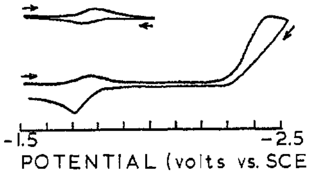

Figure 8.—Cyclic voltammograms of a 5:1 mixture of a tetraethylammonium cyanide–cobalt(II) chloride in acetonitrile containing tetraethylammonium perchlorate (1.0 × $10^{-1}$ *M*). The sweep rate is 0.2 V/sec.

**Tris(tetraethylammonium)pentacyanocobalt(II) (Ia) and Tris(tetraethylammonium)pentacyano(dioxygen)cobalt(II) Sesquihydrate (IIIb).**—Anhydrous cobalt(II) chloride (6.49 g, 0.05 mol) in deoxygenated dimethylformamide (300 ml) was added over 15 min to a well-stirred suspension of tetraethylammonium cyanide (39.0 g, 0.25 mol) in the same solvent. The resulting yellow solution was filtered and allowed to stand overnight at room

TABLE I

MAGNETIC MOMENTS OF SOLUTIONS OF TETRABUTYLAMMONIUM CYANIDE–COBALT(II) CHLORIDE MIXTURES IN ACETONITRILE, CONTAINING 1.5% TETRAMETHYLSILANE, MEASURED BY THE NMR METHOD

| $[CN^-]/[Co]$ ratio[a] | $\Delta f(Me_4Si)$,[b] Hz | $\mu_{eff}$, BM |
|---|---|---|
| 5.0 | 11.5 | 1.77 |
| 4.0 | 23 | 2.48 |
| 3.0 | 50 | 3.64 |
| 5.0[c] | 9.2 | 1.45 |

[a] $[Co] = 1.0 \times 10^{-1}\ M$. [b] $\Delta f(Me_4Si)$ = frequency difference between $Me_4Si$ resonance in paramagnetic solutions and in reference diamagnetic solutions. [c] First solution remeasured after exposure to air.

temperature. The yellow crystals (22.1 g) formed were removed by filtration (the filtrate being retained for later use), sucked dry, and then recrystallized from deoxygenated dimethylformamide (150 ml). The yellow translucent needles obtained were dried *in vacuo* to give the product (Ia) as opaque yellow needles (16.5 g, 54%).

*Anal.* Calcd for $C_{29}H_{60}CoN_8$: C, 60.0; H, 10.4; Co, 10.2; N, 19.3: Found: C, 60.3, 60.0; H, 10.7, 10.7; Co, 10.3; N, 19.2, 19.4.

The retained filtrate was removed from the drybox and allowed to stand in air for 4 days. The crystals formed were removed by filtration and dried in air to give the product (IIIa) as red-brown cubes which appear to be aggregates of plates (3.2 g, 10%).

*Anal.* Calcd, for $[(C_2H_5)_4N][Co(CN)_5O_2] \cdot 1.5H_2O$: C, 54.5; H, 10.0; N, 17.5. Found: C, 54.3, 54.5; H, 10.3, 10.4; N, 17.4, 17.6.

The esr spectrum of the solid complex Ia shows a single broad anisotropic band, centered at $g = 2.17$, and that of IIIa shows a similar band at $g = 2.02$. The infrared spectra of these two compounds are shown in Figure 12. In both Nujol mulls (NaCl or polyethylene windows) and in dimethylformamide solution (NaCl windows) $\nu$(CN) bands were observed at 2080 (Ia) and 2120 cm$^{-1}$ (IIIa).

Reaction of Ia (1.0 mmol) in dimethylformamide (20 ml) with oxygen at atmospheric pressure led to absorption of 21.3 ml (adjusted to 0°, 760 mm) of gas or 0.95 mol/mol of complex.

The electrolyte-type of compound (Ia) in water was determined by measurement of the conductivity of solutions at a series of concentrations, produced by addition of known volumes of a stock solution ($3.33 \times 10^{-2}\ M$) to pure water.

**Compound Ia.**—A solution of anhydrous cobalt(II) chloride in deoxygenated dimethylformamide ($1.0 \times 10^{-1}\ M$, 20 ml) was added to one of tetraethylammonium cyanide ($1.0 \times 10^{-1}\ M$, 100 ml) in the same solvent. Addition of ether (60 ml) precipitated a yellow solid, which was removed by filtration and washed with a dimethylformamide–ether mixture (2:1; 60 ml), followed by pure ether (3 × 60 ml). Drying *in vacuo* afforded the product as small yellow needles (1.12 g, 97%). Satisfactory analytical data were obtained for this material.

**Compound IIIa.**—Tetraethylammonium cyanide (15.6 g, 0.10 mol) was added to a stirred solution of cobalt(II) chloride (2.6 g, 0.02 mol) in dimethylformamide (500 ml). The mixture was stirred in air until all the solid had dissolved and was set aside for 3 days. The crystals formed were removed by filtration and dried *in vacuo* to give the product (7.25 g, 71%). Satisfactory analytical data, based on the sesquihydrate formulation, were obtained for this material.

**Electrochemical Reduction of Ia in Water.**—A simple U cell was used with a ground-glass fritted disk as the compartment divider. The catholyte was aqueous tetraethylammonium perchlorate ($1.0 \times 10^{-1}\ M$, 15 ml) containing complex Ia (1.16 g, 2.0 mmol); the anolyte was aqueous tetraethylammonium perchlorate ($1.0 \times 10^{-1}\ M$). A mercury cathode and platinum anode were employed, and the catholyte was stirred with a magnetic stirring bar rotating in a vertical plane at the side of the compartment. Controlled-potential reduction at $E_{cath} = -1.45$ V led to consumption of 176 C (0.91 electron/mol) and formation of a diamagnetic yellow catholyte showing a hydride resonance in its nmr spectrum.

Evaporation of the catholyte to dryness gave a yellow-gray solid which was washed with acetone until its infrared spectrum showed no perchlorate bands. The solid gave paramagnetic yellow solutions in both water and acetonitrile-$d_3$, both of which still showed the hydride resonance. On exposure of the latter solution to the air, red-brown crystals of complex IIIa precipitated which were identified by their infrared spectrum. This indicates that the ion $[HCo(CN)_5]^{3-}$ partially loses hydrogen on attempted isolation, yielding the $[Co(CN)_5]^{3-}$ ion.

**Tris(tetrabutylammonium)pentacyanocobalt(II) Hydrate (Ib) and Tris(tetrabutylammonium)pentacyano(dioxygen)cobalt(II) Sesquihydrate (IIIb).**—A solution of cobalt(II) chloride (260 mg, 2.0 mmol) in deoxygenated hexamethylphosphoramide (20 ml) was added to one of tetrabutylammonium cyanide (3.48 g, 10 mmol) in the same solvent (30 ml). The yellow solution, on standing overnight at room temperature, afforded yellow crystals which were removed by filtration and washed with hexamethylphosphoramide (2 × 5 ml) followed by ether (6 × 60 ml) and dried *in vacuo* to give the product (Ib) (1.33 g, 65%), apparently as a hydrate. *Anal.* Calcd for $C_{53}H_{110}CoN_8O$: C, 68.1; H, 11.9; N, 12.0. Found: C, 68.3, 68.4; H, 12.4, 12.7; N, 12.1, 12.2.

A similar reaction in which the yellow solution was removed from the drybox as soon as it was made up and was then allowed to stand in air for 3 days afforded the oxygenated complex IIIb (77%). *Anal.* Calcd for $C_{53}H_{111}CoN_8O_{3.5}$: C, 65.2; H, 11.5; Co, 6.0; N, 11.5. Found: C, 65.0, 65.0; H, 11.6, 11.7; Co, 6.2, 6.3; N, 11.2, 11.4.

**Pyrolysis of IIIb.**—A sample of the complex in an evacuated flask was heated at 120° for 1 hr. Examination of the gaseous products by mass spectroscopy showed them to be oxygen, carbon dioxide, and butene together with minor amounts of other hydrocarbons.

## Results and Discussion

**Conductivity Measurements.**—The partial self-ionization of cobalt(II) chloride in acetonitrile has been observed spectroscopically.[22] Thus a cobalt(II) chloride solution has a finite conductivity (Figure 1) before any cyanide is added. Apart from this deviation, the curve is almost coincident with the reference curve up to $[CN^-]/[Co] = ca.\ 3$, indicating the production of one uninegative anion for every cyanide ion added and suggesting reactions 1 and 2. Since the

$$CoCl_2 + 2CN^- \longrightarrow Co(CN)_2 + 2Cl^- \qquad (1)$$

$$Co(CN)_2 + CN^- \longrightarrow [Co(CN)_3]^- \qquad (2)$$

curves are again parallel above $[CN^-]/[Co] = ca.\ 5$, $[(C_2H_5)_4N]_3[Co(CN)_5]$ (Ia) must be the highest cyanide formed. The deviation in the curves between $[CN^-]/[Co] = 3$ and 5 may be attributed to the formation of multiply negative anions.

At the concentration used ($[Co] = 2 \times 10^{-3}\ M$), the solutions were turbid below $[CN^-]/[Co] = 3.1$–$3.2$. In the aqueous–alkali metal cation system,[23–25] turbidity, ascribed[24] to formation of polymeric $Co(CN)_2$, is observed up to $[CN^-]/[Co] = 5$ precisely. The disappearance of turbidity at lower ratios in the present system is consistent with the formation of a soluble tricyanocobalt ion (eq 2).

**Electronic Spectra.**—Aqueous solutions of $M_3[Co(CN)_5]$ (II, M = alkali metal) are green due to a band at 970 nm. Pratt and Williams[23] have interpreted this as evidence that the ion present is actually $[Co(CN)_5H_2O]^{3-}$ and infer that it would be absent if the ion were truly pentacoordinate. This interpretation has been disputed,[9,10,26] and it has been shown[9] that if the ion is produced by electron irradiation of solid (and presumably anhydrous) $K_6[Co(CN)_6]$, then this band is still present. Nevertheless, in the present

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[22] W. Libus, *Rocz. Chem.*, **36**, 999 (1962).

[23] J. M. Pratt and R. J. P. Williams, *J. Chem. Soc. A*, 1291 (1967).

[24] J. Halpern and M. Pribanić, *J. Amer. Chem. Soc.*, **93**, 96 (1971).

[25] D. N. Hume and I. M. Kolthoff, *ibid.*, **71**, 867 (1949).

[26] K. G. Caulton, *Inorg. Chem.*, **7**, 352 (1968).

anhydrous system, at $[CN^-]/[Co] = 5$, the band is not observed and the solutions are yellow. Similar solutions in water are green and do show this band. These results appear to favor the arguments of Pratt and Williams[23] as to that nature of the pentacyanocobalt ion in aqueous solution. A band at 285 nm observed (Figure 2) in solutions with $[CN^-]/[Co] = 4$ and 5 may be attributed to the $[Co(CN)_5]^{3-}$ ion and is similar in wavelength to the 280-nm band of aqueous solutions of II. At the low concentration used ($[Co] = 2 \times 10^{-4}$ *M*), the solutions were clear even at $[CN^-]/[Co] = 2$ and, at that ratio, a band at 605 nm is observed (Figure 3). On the basis of its wavelength and extinction coefficient[27] (*ca.* 500) and its similarity to a band observed in hexamethylphosphoramide solutions,[17] this may be attributed to $(CH_3CN)_2Co(CN)_2$.

Gutmann and his coworkers have postulated the formation of a tricyanocobalt species in hexamethylphosphoramide[19] and a tetracyanocobalt species in nitromethane[16] as the intermediate stage between $Co(CN)_2$ and $[Co(CN)_5]^{3-}$, whereas in other solvents[17,18] no evidence was found for any species intermediate between these two. In the present case, the spectra (Figure 3) show clearly an intermediate tetrahedral species with a structured band at about 590 nm and a strong charge-transfer band at 250 nm. At $[CN^-]/[Co] = 4$ (Figure 2), the former band is apparently lost in the tail of the ultraviolet bands of $[Co(CN)_5]^{3-}$ now present in appreciable quantity, but the charge-transfer band is visible. An expanded spectrum of the ultraviolet bands (Figure 4) shows two points which are very nearly isosbestic, suggesting that above $[CN^-]/[Co] = 3.5$ the intermediate tetrahedral species and the $[Co(CN)_5]^{3-}$ ion are the only complexes present in appreciable quantity.

Further study has been made of the band due to the $[Co(CN)_5]^{3-}$ ion at 285 nm. A plot of its apparent extinction coefficient against $[CN^-]/[Co]$ ratio is shown (Figure 5) and indicates that dissociation of the $Co(CN)_5{}^{3-}$ ion is extensive at this low concentration ($2 \times 10^{-4}$ *M*), even above $[CN^-]/[Co] = 5$. Dissociation of II in aqueous solutions has been observed[23,28] but appears less extensive; this may be an effect of the relative dielectric constants of acetonitrile (36.7)[29] and water (78.5).[30]

**Electrochemical Measurements.**—Aqueous solutions of II show a polarographic wave with $E_{1/2} = -1.3$ V *vs.* sce (saturated calomel electrode) due to the process shown (eq 3).[25] At $[CN^-]/[Co] = 4.5$–5, a kinetic prewave is observed[31,32] with $E_{1/2} = -1.1$ V.

$$H_2O + [Co(CN)_5]^{3-} + e^- \longrightarrow [Co(CN)_5H]^{3-} + OH^- \quad (3)$$

In the present system, at $[CN^-]/[Co] = 5$, two reduction waves are observed (Figure 7) with $E_{1/2} = -2.4$ V (A) and $-1.8$ V (B). The height of both waves increases linearly with concentration as does that of the oxidation wave (C) which is also observed. At $[CN^-]/[Co] = 6$, the large oxidation wave which carries the curve off scale is due to oxidation of free cyanide ion. Wave C may also be due to oxidation of cyanide ion, but it has not been further investigated. The variation in the relative heights of the reduction waves with $[CN^-]/[Co]$ ratio (Figure 7) indicates that they are due to reduction of $[Co(CN)_5]^{3-}$ (wave A) and of a product formed by dissociation of this ion (wave B).

At $[CN^-]/[Co] = 4$, the approximate equivalence of the heights of waves A and B indicates that the dissociated species is a tricyanocobalt ion (at this ratio both waves are diffusion controlled, their heights being proportional to $\sqrt{h}$; $h$ = height of the mercury column[33]). This is in agreement with the conductivity data detailed above which indicated the formation of such an anion. Presumably this ion is the intermediate tetrahedral species detected by its ultraviolet band at 250 nm (Figure 4), and it is thus formulated as $[CH_3CNCo(CN)_3]^-$. At $[CN^-]/[Co] = 5$, wave B is independent of $h$ and is a kinetic wave.[34] Although a similar wave is observed in the aqueous–alkali metal cation system, it is much closer to the $Co(CN)_5{}^{3-}$ wave and is assigned to a tetracyanocobalt ion.[31,32] Since wave B is kinetic at $[CN^-]/[Co] = 5$, the relative wave heights are not an indication of the relative concentration of the two complexes at this ratio, wave B being much higher than would be expected for the actual concentration of $[CH_3CNCo(CN)_3]^-$.

Cyclic voltammograms (Figure 8) of a solution with $[CN^-]/[Co] = 5$ show two reduction peaks corresponding to waves A and B, with $E_{p,c} = -2.4$ V and $E_{p,c} = -1.75$ V, the latter displaying a reverse with $E_{p,a} = -1.7$ V. The reverse oxidation peak is increased in size if the forward sweep is carried through the region of reduction of $[Co(CN)_5]^{3-}$. Thus, both $[Co(CN)_5]^{3-}$ and $[CH_3CNCo(CN)_3]^-$ are reduced to the same species; since the reduction of the latter is reversible, the species must be $[CH_3CNCo(CN)_3]^{2-}$. The loss of cyanide on reduction of $(R_4N)_3[Co(CN)_5]$ in acetonitrile contrasts with reported[35] *reversible* reduction of $K_3[Co(CN)_5]$ in water at very high pH. The $[Co(CN)_5]^{4-}$ ion formed has also been observed as a transient intermediate in the reaction of aqueous II with hydrated electrons.[36] The cyanide loss in the present system may again be an effect of the lower dielectric constant of the organic solvent.

**Magnetic Measurements.**—Magnetic moment measurements by the method of Evans[37,38] (Table I) show the expected[39] spin-only value (within experimental error) at $[CN^-]/[Co] = 5$ and higher values at lower ratios. The latter must be due to the increasing presence of $[CH_3CNCo(CN)_3]^-$ and show it to be a high-spin species.

Final confirmation of the presence of the ions $[Co(CN)_5]^{3-}$ and $[CH_3CNCo(CN)_3]^-$ is afforded by the esr spectra of solutions with $[CN^-]/[Co] = 5$ and 3 (Figures 9 and 10). Both indicate axially symmetric

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(27) R. L. Carlin, *Transition Metal Chem.*, **1**, 1 (1964).

(28) T. Susuki and T. Kwan, *J. Chem. Soc. Jap.*, **87**, 395 (1966).

(29) T. C. Waddington, "Nonaqueous Solvents," Academic Press, New York, N. Y., 1965.

(30) R. C. Weast and S. M. Selby, "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, Ohio, 1967.

(31) H. Matschiner, Thesis, Martin Luther University, Halle-Wittenberg, 1963.

(32) H. S. Lim and F. C. Anson, paper submitted for publication.

(33) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience, New York, N. Y., 1952, p 85.

(34) Reference 33, pp 268–281.

(35) J. Hanzlick and A. A. Vlček, *Chem. Commun.*, 47 (1969).

(36) G. D. Venerable and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 2176 (1971).

(37) D. F. Evans, *J. Chem. Soc.*, 2003 (1969).

(38) H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).

(39) G. A. Mills, S. Weller, and A. Wheeler, *J. Phys. Chem.*, **63**, 403 (1959).

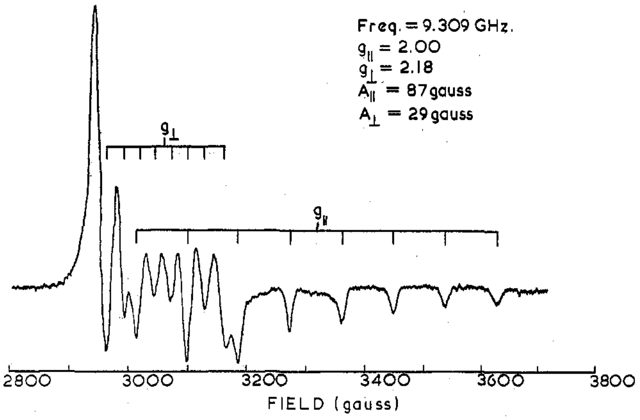

Figure 9.—The esr spectrum of a 5:1 mixture of tetraethylammonium cyanide and cobalt(II) chloride in acetonitrile at 77°K, [Co] $= 2 \times 10^{-2}$ *M*.

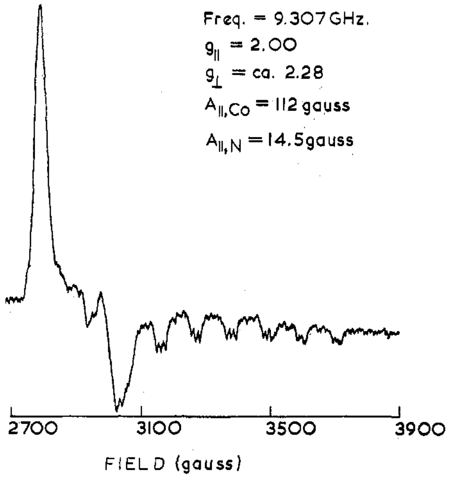

Figure 10.—The esr spectrum of a 3:1 mixture of tetraethylammonium cyanide and cobalt(II) chloride in acetonitrile at 77°K, [Co] $= 2 \times 10^{-2}$ *M*.

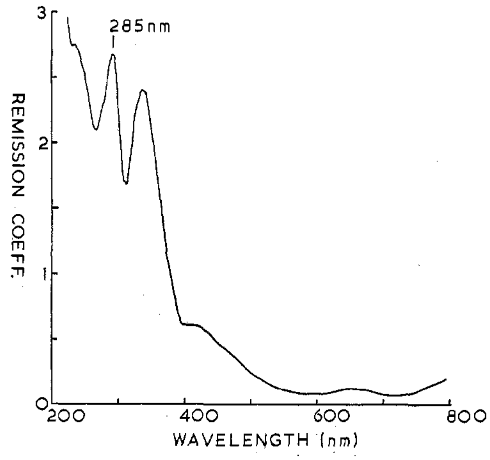

Figure 11.—Diffuse reflectance spectrum of Ia measured on a powdered mixture of equal weights of Ia and lithium fluoride.

species, the former being very similar to that reported[9,10,40] for aqueous solutions of II. The additional 1:1:1 triplet splitting ($^{14}$N, $S = 1$) in the $g_{\|}$ octet ($^{59}$Co, $S = {}^7/_2$) of the latter confirms the presence of coordinated acetonitrile on the axis of symmetry in $[CH_3CNCo(CN)_3]^-$.

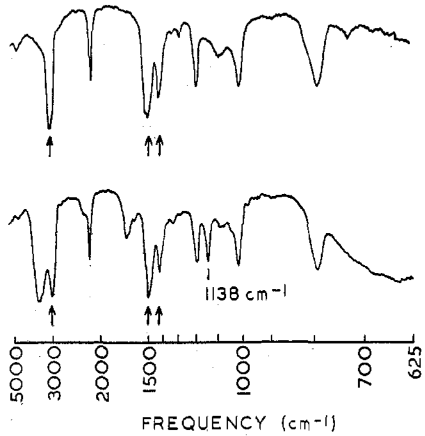

Figure 12.—Infrared spectra of compounds Ia (upper) and IIIa (lower), obtained as Nujol mulls between sodium chloride plates. The arrows denote bands due to Nujol.

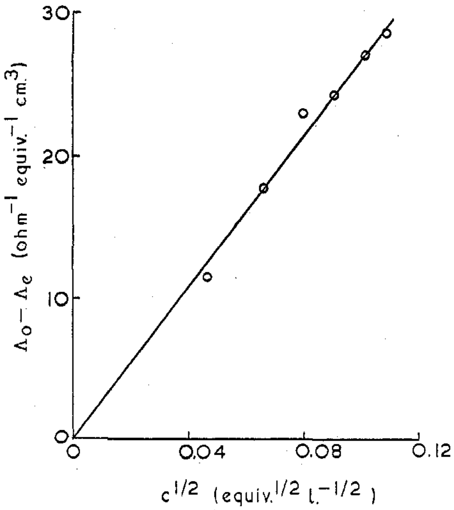

Figure 13.—The dependence of $\Lambda_0 - \Lambda_e$ ($\Lambda_e$ = equivalent conductivity; $\Lambda_0$ = that at infinite dilution) of compound Ia on concentration ($\sqrt{c}$), measured in water, at room temperature (*ca.* 24°).

**Isolation and Reactions of $(R_4N)_3[Co(CN)_5]$ (I).**—We have found that $[(C_2H_5)_4N]_3[Co(CN)_5]$ (Ia) may be easily obtained from dimethylformamide solutions either by precipitation with ether or by crystallization from sufficiently concentrated solutions. In the latter case, long translucent yellow needles are initially formed, but on filtration they apparently lose solvent, even at atmospheric pressure, giving the solvent-free material as an opaque yellow solid which retains the original needle form. The tetrabutylammonium salt Ib similarly obtained from hexamethylphosphoramide solutions behaves in the same way but appears to be a monohydrate.

Compound Ia is paramagnetic, giving a strong broad signal at $g = 2.17$ in the solid state. On dissolution in acetonitrile, the previously observed esr (Figure 9) and electronic spectra [Figure 2, curve a] are regenerated. Its electronic spectrum in the solid state (Figure 11) is similar to that in solution. Its infrared spectrum (Figure 12) shows a $\nu$(CN) band at 2080 cm$^{-1}$, comparable with that reported[41] for aqueous solutions of II (2083 cm$^{-1}$). It gives yellow solutions in acetonitrile

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[40] M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc. A*, 2069 (1971).

[41] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **87**, 5361 (1965).

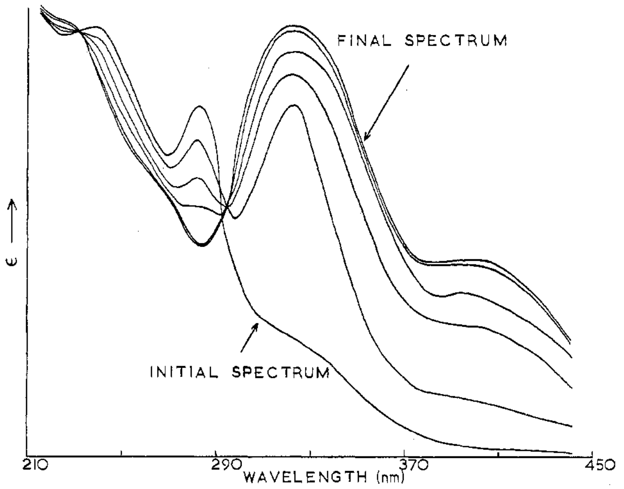

Figure 14.—Ultraviolet spectral behavior of an acetonitile solution of a 5:1 mixture of a tetrabutylammonium cyanide–cobalt(II) chloride mixture on exposure to air, [Co] = $2.0 \times 10^{-4}$ *M*. Scans were started at 60-sec intervals, the first one being made *ca.* 60 sec after exposure to air. The scan duration was *ca.* 35 sec.

and dimethylformamide and green solutions in water. An electrolyte-type determination by the method of Feltham and Hayter[42] gives a plot of $\Lambda_0 - \Lambda_e$ *vs.* $\sqrt{c}$ (Figure 13) which has a slope of 285. This value is typical of a 3:1 electrolyte and indicates that the ion is monomeric in aqueous solution. In contrast to its very cathodic reduction potential in acetonitrile ($E_{1/2} = -2.4$ V), compound Ia shows a single polarographic reduction wave at −1.45 V in water, and bulk electrolysis affords the ion $[Co(CN)_5H]^{3-}$. This species was identified in solution by its diamagnetism and hydride resonance at 1045 Hz above the water resonance (measured at 60 MHz, comparable with literature[12,43] values for the alkali metal salts), but it partially decomposed, giving Ia again on attempted isolation. Although cyclic voltammetry in acetonitrile indicates the formation of $[CH_3CNCo(CN)_3]^{2-}$ which is stable on the electrode surface, this species could not be isolated by reduction in that solvent. A transient blue color, which dissipated on shutting off the current, was observed and may be attributed to it, but the nature of the final product is not known. It was established that $[Co(CN)_5H]^{3-}$ was not formed.

Compounds I are very air sensitive as illustrated by Figure 14. This spectral change is accompanied by a small decrease in magnetic moment (Table I) and an uptake of about 1 mol of oxygen/mol of complex. From concentrated solutions, red-brown crystals separate; after filtration and air-drying (associated solvent appears to be replaced by water in this process), the compounds $(R_4N)_3[Co(CN)_5O_2]\cdot 1.5H_2O$ (III) are obtained.

| $(R_4N)_3]Co(CN)_5]$ | $(R_4N)_3[Co(CN)_5O_2]\cdot 1.5H_2O$ |
|---|---|
| Ia, R = $C_2H_5$ | IIIa, R = $C_2H_5$ |
| b, R = $n$-$C_4H_9$ | b, R = $n$-$C_4H_9$ |

The esr spectrum of both solid compounds III consists of a broad signal, showing no hyperfine structure and centered at $g = 2.02$–$2.03$ when measured on the solid or in acetonitrile, but in acetone solution, an eight-line resonance (Figure 15) is observed. The latter spectrum is very similar to that observed[44] for a *transient* intermediate in the reaction of aqueous solutions of II with oxygen ($g = 2.01$, $A_{Co} = 9.8$ G)[45] and ascribed to the $[Co(CN)_5O_2]^{3-}$ ion. It is also very similar to the spectra of a class of monomeric cobalt–oxygen complexes prepared in recent years[46–54] and these similarities leave no doubt that compounds III are members of this class. In this case, however, the oxygenation reaction is not reversible, but the oxygen can be liberated by pyrolysis of the isolated solid. Products ($CO_2$ and butene from IIIb) which appear to be due to degradation of the cation are also formed.

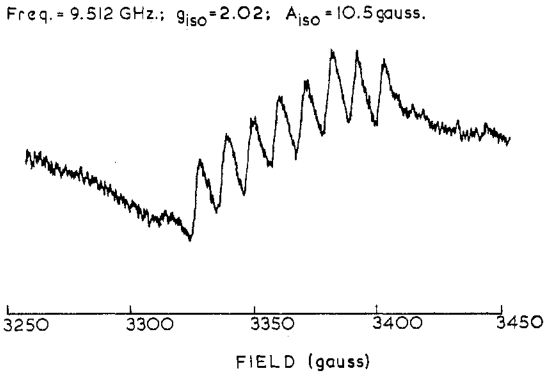

Figure 15.—The esr spectrum of compound IIIb in acetone at room temperature, [Co] = $2 \times 10^{-2}$ *M*.

The infrared spectrum of compound IIIa is shown in Figure 12 and exhibits $\nu(C{\equiv}N)$ at 2120 cm$^{-1}$ which lies in the range expected for cobalt(III) ions of the type $[Co(CN)_5X]^{3-}$ (2096–2134 cm$^{-1}$).[41] Apart from the bands due to water, the spectrum of IIIa shows one band not present in that of Ia (at 1138 cm$^{-1}$), which lies in the range (1120–1140 cm$^{-1}$) in which $\nu$(O–O) occurs for other similar compounds.[46b,48]

One of the most characteristic reactions of aqueous solutions of II is their reaction with hydrogen to give the ion $[HCo(CN)_5]^{3-}$. With solutions containing [Co] = *ca.* $10^{-1}$ *M*, this reaction is complete at atmospheric pressure within minutes, but, under the same conditions, compound Ia in acetonitrile was unchanged after several hours. In aqueous solutions of II, Halpern and Pribanić[55] have shown that this reaction is either termolecular or involves prior dimerization of the pentacyanocobalt ion followed by a rate-determining reaction with hydrogen. The former mechanism is preferred on the basis that its transition state resembles the final state more than does that of the latter process.

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(42) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4857 (1964).

(43) W. P. Griffith and G. Wilkinson, *ibid.*, 2757 (1959).

(44) J. H. Bayston, F. D. Looney, and M. E. Winfield, *Aust. J. Chem.*, **16**, 557 (1963).

(45) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969).

(46) (a) B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, **92**, 61 (1970); (b) A. L. Crumbliss and F. Basolo, *ibid.*, **92**, 55 (1970).

(47) D. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Commun.*, 467 (1970).

(48) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1949).

(49) H. Kon and N. E. Sharpless, *Spectrosc. Lett.*, **1**, 49 (1968).

(50) S. A. Cockle, H. A. O. Hill, and R. J. P. Williams, *Inorg. Nucl. Chem. Lett.*, **6**, 131 (1970).

(51) S. Koda, A. Misono, and Y. Uchida, *Bull. Chem. Soc. Jap.*, **43**, 3143 (1970).

(52) G. Costa, A. Puxeddu, and L. B. Stefani, *Inorg. Nucl. Chem. Lett.*, **6**, 191 (1970).

(53) N. L. Yang and G. Oster, *J. Amer. Chem. Soc.*, **92**, 5265 (1970).

(54) E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nucl. Chem. Lett.*, **7**, 901 (1971).

(55) J. Halpern and M. Pribanić, *Inorg. Chem.*, **9**, 2616 (1970).

However, whichever mechanism is operative, two pentacyanocobalt ions must come close together. The lack of reaction in the present system may indicate that this approach is not possible because of the bulkiness of the tetraalkylammonium cations. This effect may also rationalize two other major differences between the two systems. First, compounds I show no tendency to dimerize either in concentrated solution or in the solid state. In fact, analogs of the compounds $M_6[Co_2(CN)_{10}]\cdot xH_2O$ have not been observed in the present system, whereas all previous attempts to obtain the monomeric ion, except the one report of Pregaglia and coworkers,[12] have given these dimers. It is notable that lithium is the cation in the one previous exception. The high charge/radius ratio of this ion promotes ion pairing which might hinder dimerization. Also, the acetone and ethanol observed in their product are most probably associated with the cation, thus giving it a large effective size and, thereby, further obstructing close approach of two anions. Secondly, the solutions of I in acetonitrile and of II in water differ in their reaction with oxygen in that, in the latter case, the dinuclear complex ion $[(CN)_5CoOOCo(CN)_5]^{6-}$ is produced,[44] whereas in the former the reaction stops at $[Co(CN)_5O_2]^{3-}$, which has been observed[44] as an intermediate in the formation of the dinuclear complex. Again, the lack of formation of a dinuclear complex may be attributed to the inability of two ions to come in close contact due to the bulkiness of the cations.

Although the ion $[Co(CN)_5H]^{3-}$ is not obtainable by reaction of Ia with hydrogen, it is formed on electrochemical reduction of its aqueous solutions. It is notable that in this case the mechanism consists of addition of an electron followed or accompanied by a bimolecular reaction with water; *i.e.*, it does not require close approach of two anions.

We have observed that acetonitrile solutions of Ia react with benzoquinone to give dark diamagnetic solutions, presumably containing benzoquinone-bridged anions reported by Vlček and Hanzlik.[56] Diamagnetic solutions were also obtained on reaction with halogens and with allylic halides in acetonitrile, again suggesting reactions similar to those observed[6] for aqueous solutions of II.

**Acknowledgments.**—The authors are indebted to Professor F. C. Anson for the preprints of two papers on the pentacyanocobalt(II) ion and for the loan of a copy of Matschiner's thesis,[31] to Dr. M. Takano for a translation of a paper[28] in Japanese, and to Dr. P. A. Berger for running the esr spectra.

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(56) A. A. Vlček and J. Hanzlik, *Inorg. Chem.*, **6**, 2053 (1967).

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# Ionization Equilibria in Anhydrous Cobalt(II) Chloride–Acetonitrile

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Independent investigators have studied the anhydrous $CoCl_2$–$CH_3CN$ system and have arrived at somewhat ambiguous results. Janz and coworkers have proposed the existence of a neutral dimer, $(CoCl_2\cdot 3L)_2$, which dissociates into $CoL_6^{2+}$ and $CoCl_4^{2-}$, where L = $CH_3CN$. Libus and coworkers denied the existence of dimeric species and proposed that dissociation produces $CoL_6^{2+}$ and $CoCl_3L^-$, where again L = $CH_3CN$. In the present investigation, effective molecular weights and visible absorption spectra indicate that the ionic dimer $(CoCl_3^-)_2$ is formed in significant amounts in the system. It is also observed that the formation of this dimeric species is facilitated by the addition of salts such as $Et_4NCl$ or LiCl that furnish additional chloride ions to the acetonitrile medium and that the dimerization is independent of the size of the cation associated with the added chloride salt.

## Introduction

The anhydrous system composed of $CoCl_2$ and $CH_3CN$ has been studied by independent investigators in an attempt to identify the ionic and molecular species in the system and also to establish the nature of the equilibrium processes responsible for the existence of these species. On the basis of electrical conductance data, solid substrate analysis, and visible absorption spectra, Janz[1] proposed the following model as a description of the ionization processes operating in the anhydrous system, where L = $CH_3CN$

$$2CoCl_2 + 6L \rightleftarrows (CoL_6{}^{2+}CoCl_4{}^{2-}) \qquad (1)$$

$$(CoL_6{}^{2+}CoCl_4{}^{2-}) \rightleftarrows CoL_6{}^{2+} + CoCl_4{}^{2-} \qquad (2)$$

$$(CoL_6{}^{2+}CoCl_4{}^{2-}) + 2L \rightleftarrows CoL_6{}^{2+} + CoCl_4L_2{}^{2-} \qquad (3)$$

In a separate study, Libus[2] concluded, on the basis of visible absorption spectra, that the following model is a better description of the system where again L = $CN_3CN$

$$CoCl_2 + 2L \rightleftarrows CoCl_2L_2 \qquad (4)$$

$$3CoCl_2L_2 + 2L \rightleftarrows CoL_6{}^{2+} + 2CoCl_3L^- \qquad (5)$$

The basic differences in these two models lie in the fact that a dimeric species was proposed by Janz, while no monomer–dimer equilibrium was predicted by Libus, and in the fact that Janz identified the major anionic species present as $CoCl_4^{2-}$, while Libus reported the predominant anion as $CoCl_3L^-$.

In the present investigation, the apparent molecular weight of $CoCl_2$ in $CH_3CN$ is determined by vapor pressure osmometry, in both the presence and absence of additional chloride ion. These data are correlated with visible absorption spectra in an attempt to reconcile the controversy surrounding the existence of a monomer–dimer equilibrium and to provide further

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(1) G. J. Janz, A. E. Marcinkowsky, and H. V. Venkatasetty, *Electrochim. Acta*, **8**, 867 (1963).

(2) W. Libus, *Rocz. Chem.*, **36**, 999 (1962).