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Reactions of Nitrosyl Chloride with Some Transition Metal–Cyano Complexes in Selected Nonaqueous Media

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The behavior of nitrosyl chloride toward a number of transition metal–cyano complexes in either tetrahydrothiophene 1,1-dioxide (sulfolane, $TMSO_2$) or N,N-dimethylformamide (DMF) has been investigated. Where reaction occurs, nitrosyl chloride functions solely as a one-electron oxidant; in no case is NO found as a ligand in the products isolated. Of particular interest are the following conversions: $K_2Mo^{III}(CN)_5 \rightarrow K_3Mo^{III}Mo^{IV}(CN)_{10}$; $K_2Mn^{II}[Mn^{II}(CN)_6] \rightarrow KMn^{II}[Mn^{III}(CN)_6]$; $K_3[Mn^{III}(CN)_6] \rightarrow K_2[Mn^{IV}(CN)_6]$. The last transformation apparently provides the first unequivocal preparation of a manganese(IV)–cyano complex.

The stimulus for the work described in this paper was a report by Seel and coworkers[1] on the reactions between nitrosyl chloride and the complex thiocyanates $K[Cr(NCS)_4(NH_3)_2]$ and $K_3[Cr(NCS)_6]$ in liquid sulfur dioxide. In each case, potassium was precipitated as the chloride and nitric oxide was evolved. From the former reaction, there was isolated a substance formulated as $[Cr(NCS)_3(NH_3)_2]_2(NCS)_2$, which in refluxing nitromethane was converted to $[Cr(NCS)_3(NH_3)_2]_2$ and polythiocyanogen. Chromium(III) thiocyanate and polythiocyanogen were obtained from the hexathiocyanato complex. In effect, the nitrosyl chloride functioned as an oxidant toward the thiocyanate ligand.

It was hoped that with transition metal complexes having ligands less susceptible to oxidation than thiocyanate, nitrosyl chloride would function as an oxidant toward the central metal atom and thus provide a route to higher oxidation states. A number of cyano complexes were chosen for investigation. The reaction medium was either tetrahydrothiophene 1,1-dioxide ($TMSO_2$) or N,N-dimethylformamide (DMF). Where solubility factors were favorable, $TMSO_2$ proved to be a more useful solvent than DMF, since it had a much smaller tendency to solvate strongly with products of reaction.

Experimental Section

Materials.—Nitrosyl chloride, of a stated purity of 97%, was purchased from the Matheson Co. and was condensed as needed directly from the commercial cylinder. Nitrogen, the source of which was Linde or Air Products Co., was purified prior to use by passage over hot copper metal. The following reagent grade solvents were employed without further purification: N,N-dimethylformamide (Fisher and also Baker & Adamson), anhydrous ethyl ether (Baker & Adamson), and acetone (J. T. Baker). Anhydrous methanol and ethanol were obtained from the commercial materials, the former by distillation from magnesium methoxide and the latter by distillation from magnesium ethoxide. Tetrahydrothiophene 1,1-dioxide, obtained from Distillation Products (Eastman), was purified by vacuum distillation from 40-mesh calcium hydride. The purity of the product was established by the melting point of the distillate, 28–29°. Potassium hexacyanochromate(III) was synthesized by the method of Bigelow.[2] The yellow salt was recrystallized twice by dissolving it in water and reprecipitating with ethanol. The product was dried *in vacuo* at 100°. *Anal.* Calcd for $K_3[Cr(CN)_6]$: Cr, 15.98. Found: Cr, 15.89. Potassium octacyanomolybdate(IV) was prepared from molybdenum(VI) oxide according to the directions of Furman and Miller.[3] The yellow salt was purified three times by dissolution in a minimum amount of warm water (50°) and reprecipitation by the addition of ethanol. The final product was washed with ethanol and ether and dried under vacuum at 110°. *Anal.* Calcd for $K_4[Mo(CN)_8]$: Mo, 20.84. Found: Mo, 20.74. Potassium hexacyanomolybdate(II) was obtained from the octacyanomolybdate(IV) complex by reduction with hydrogen at elevated temperatures as described by Yoo, Griswold, and Kleinberg.[4] The infrared spectrum of the product matched that previously reported. *Anal.* Calcd for $K_4[Mo(CN)_6]$: Mo, 23.49. Found: Mo, 23.25. Potassium pentacyanomolybdate(III) was made from the octacyanomolybdate(IV) by the method of Magnuson, Griswold, and Kleinberg employing molten potassium cyanide both as reductant and reaction medium.[5] The infrared spectrum of the material isolated was identical with that cited by Magnuson, *et al.* *Anal.* Calcd for $K_2Mo(CN)_5$: Mo, 31.54. Found: Mo, 31.42. The procedure of Heintz[6] was used for the preparation of potassium octacyanotungstate(IV) from $K_3[W_2Cl_9]$. The pale yellow cyano complex was recrystallized

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[1] F. Seel, A. Hauser, and D. Wesemen, *Z. Anorg. Allgem. Chem.*, **283**, 351 (1956).

[2] J. H. Bigelow, *Inorg. Syn.*, **2**, 203 (1946).

[3] N. H. Furman and C. O. Miller, *ibid.*, **3**, 169 (1950).

[4] J. S. Yoo, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **4**, 365 (1965).

[5] W. L. Magnuson, E. Griswold, and J. Kleinberg, *ibid.*, **3**, 88 (1964).

[6] E. A. Heintz, *Inorg. Syn.*, **7**, 142 (1963).

three times from aqueous solution by precipitation with 95% ethanol. This procedure yielded the dihydrate. *Anal.* Calcd for $K_4[W(CN)_8]\cdot 2H_2O$: K, 26.76; W, 31.46. Found: K, 27.45; W, 31.80. The product was converted to the anhydrous complex by drying *in vacuo* at 110°. Potassium hexacyanotungstate(II) was obtained by a method analogous to that used for the corresponding molybdenum compound.[4] *Anal.* Calcd for $K_4[W(CN)_6]$: W, 37.04. Found: W, 36.82. The procedure reported by Lower and Fernelius[7] was used for the synthesis of potassium hexacyanomanganate(III) from manganese(III) orthophosphate and potassium cyanide. The red crystalline product was dried under vacuum at 110° to ensure complete removal of adsorbed water. *Anal.* Calcd for $K_3[Mn(CN)_6]$: Mn, 16.73. Found: Mn, 16.68. Potassium tricyanomanganate(II) ($K_2Mn^{II}[Mn^{II}(CN)_6]$) was made by the slow addition of an aqueous solution of potassium cyanide to one of manganese(II) acetate according to the directions of Straus.[8] The resulting green precipitate was collected by suction filtration, washed thoroughly with water and ethanol, and dried *in vacuo* at 110°. *Anal.* Calcd for $KMn(CN)_3$: Mn, 31.92. Found: Mn, 31.29. Potassium hexacyanoferrate(II) was obtained by drying a finely powdered sample of the commercial dihydrate (99.99% stated purity) at 110° under vacuum. The corresponding iron(III) complex (99.99% stated purity) was purchased from the J. T. Baker Chemical Co. and used without further treatment. Potassium decacyanodicobaltate(II) was synthesized by the method of Adamson.[9] The product was dried *in vacuo* over P_4O_{10} at room temperature. *Anal.* Calcd for $K_6[Co_2(CN)_{10}]$: Co, 19.24. Found: Co, 18.90. Thermal treatment of this compound as described by Reinstein, Griswold, and Kleinberg[10] yielded the monomer potassium pentacyanocobaltate(II). *Anal.* Calcd for $K_3[Co(CN)_5]$: Co, 19.24. Found: Co, 18.90. The procedure of Fernelius and Burbage[11] was employed for the preparation of potassium tetracyanonickelate(II). The final product was powdered and then dried under vacuum at 110°. *Anal.* Calcd for $K_2[Ni(CN)_4]$: Ni, 24.36. Found: Ni, 23.64. Potassium hexacyanodinickelate(I) was made as described by Malatesta and Pizzotti.[12] The product after having been dried *in vacuo* at room temperature was stored under nitrogen. *Anal.* Calcd for $K_4[Ni_2(CN)_6]$: Ni, 27.31. Found: Ni, 26.83.

Analytical Procedures.—The potassium content of the various starting materials and products was determined gravimetrically by precipitation as the tetraphenylborate from acidic solution.[13] Potassium-containing materials which were water insoluble were prepared for analysis by decomposing them in basic solution with calcium hypochlorite.[14] The percentage of cyanide in a sample was determined by one of several methods. Where there apparently was no bridging cyanide present, the modified Kjeldahl procedure for nitrogen described by Jaselski and Lanese[15] generally proved satisfactory. Also employed were a sodium fusion procedure,[16] microanalysis for carbon and nitrogen,[17] and the method of Williams,[18] which is based largely on the conversion of cyanide to the free acid in the presence of copper(I) chloride; ammonium ion formed in a small amount as a hydrolytic product is also determined. Molybdenum or tungsten was analyzed for by precipitation of the 8-hydroxyquinolate after the sample had been decomposed and the metal oxidized to the hexapositive state.[19] Manganese was determined as the bipositive ion by titration with standardized 0.1 *N* EDTA in the presence of Eriochrome Black T indicator.[20] In the analysis for cobalt, the element was precipitated quantitatively as tetrapyridinedithiocyanatocobalt(II).[21] Nickel was obtained titrimetrically with EDTA as titrant and murexide as indicator.[22]

Infrared Spectra.—Such spectra were recorded in the region from 4000 to 650 cm^{-1} with a Perkin-Elmer Model 421 grating spectrometer. The solid sample was dispersed in a Nujol or halocarbon mull.

Magnetic Susceptibility Measurements.—These measurements were made at room temperature, *ca.* 25°, by either the Gouy or Faraday method, using the susceptibility of $Hg[Co(NCS)_4]$ as a standard. Diamagnetic corrections were calculated with the use of constants listed by Selwood.[23]

General Outline of Experimental Procedure for Reactions.—The reaction flask was a 250-ml, round-bottomed flask fitted with three standard-taper 24/40 female joints. One entry of the flask was connected to a vacuum pump through a stopcock; the middle entry was fitted with a tube connected to a liquid nitrogen trap; a curved delivery tube passed through the third entry and reached almost to the bottom of the flask. The delivery tube was joined, through a 9/18 ball joint and a stopcock, to a calibrated (roughly) condensation bulb, and the latter was connected to sources of nitrogen and nitrosyl chloride through a three-way stopcock. The reaction flask contained a Teflon-coated spin bar for magnetic stirring and the joints were fitted with Teflon sleeves to prevent seizure and to avoid contamination of the reaction mixture by silicone grease.

In a typical reaction, solvent (30–60 ml) was placed in the reaction flask and the system was deaerated for about 20 min with nitrogen while the solvent was stirred magnetically. The nitrogen flow was then decreased and a weighed sample (generally 2–5 g) of the complex to be studied was introduced into the flask through the central neck by removal of the inner joint. The joint was replaced and the nitrogen flow increased. After about 5 min, the flow of nitrogen was halted, and the three-way stopcock was adjusted to permit the entry of nitrosyl chloride. A 3–5-fold molar excess of this gas (relative to the complex) was liquefied in the condensation bulb with the aid of a Dry Ice–2-propanol bath. A slow stream of nitrogen was then started, the stopcock leading to the reaction flask *via* the delivery tube was opened, and the liquid nitrosyl chloride was warmed with the hand until all of it had bubbled slowly into the solvent in the reaction flask. If reaction with the complex occurred, the formation of small bubbles on the bottom of the flask and vigorous evolution of a colorless gas on the surface of the liquid were noted immediately. The gas formed was shown to be nitric oxide by allowing some of it to pass first through the liquid nitrogen trap to remove nitrosyl chloride and then through an acidified solution of iron(II) sulfate, with which it reacted to give the characteristic brown solution. (The gas was also identified as nitric oxide by observing its reaction with the atmosphere to form the dioxide.) Reaction of nitrosyl chloride with the complex was considered to be complete when vigorous gas evolution ceased. At this point the reaction mixture was generally stirred for 15–20 min while a slow stream of nitrogen was passed through. The gas delivery tube and the trap assembly were then replaced with glass stoppers fitted with Teflon sleeves and the excess nitrosyl chloride which was dissolved in the solvent was removed by evacuating the reaction flask. Pumping was continued for 15–20 min, after which the reaction flask was disconnected from the vacuum line and filled with nitrogen. The reaction mixture was then worked up in the manner appropriate for each starting complex. Infrared, magnetic susceptibility, and elemental analytical data were obtained for the products.

Most of the reactions were also carried out in the presence of potassium cyanide to determine whether excess ligand had any

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(7) J. A. Lower and W. C. Fernelius, *Inorg. Syn.*, **2**, 213 (1946).

(8) P. Straus, *Z. Anorg. Allgem. Chem.*, **9**, 6 (1895).

(9) A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

(10) J. G. Reinstein, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **8**, 2499 (1969).

(11) W. C. Fernelius and J. J. Burbage, *Inorg. Syn.*, **2**, 227 (1946).

(12) L. Malatesta and R. Pizzotti, *Gazz. Chim. Ital.*, **72**, 174 (1942).

(13) K. Sporek and A. F. Williams, *Analyst*, **80**, 347 (1955).

(14) D. F. Banks, Ph.D. Thesis, University of Kansas, 1967, p 70.

(15) B. Jaselski and J. G. Lanese, *Anal. Chim. Acta*, **23**, 6 (1960).

(16) J. G. Reinstein, Ph.D. Thesis, University of Kansas, 1969, pp 21–22.

(17) Performed by Mrs. G. Kristiansen, Department of Medicinal Chemistry, University of Kansas.

(18) H. E. Williams, *J. Soc. Chem. Ind., London*, **31**, 468 (1912).

(19) L. Erdey, "Gravimetric Analysis," Part II, Pergamon Press, New York, N. Y., 1965, pp 535, 550.

(20) H. A. Flaschka, "EDTA Titrations," Pergamon Press, New York, N. Y., 1964, p 81.

(21) Reference 19, p 409.

(22) Reference 20, p 83.

(23) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1956, p 78.

effect on the nature of the product. In no instance was any difference observed.

The behavior of the following complexes toward nitrosyl chloride was investigated (solvent in parentheses): $K_3[Cr(CN)_6]$ ($TMSO_2$), $K_3[Fe(CN)_6]$ (DMF), $K_3[Co(CN)_6]$ (DMF), $K_4[Mo(CN)_8]$ ($TMSO_2$), $K_4[Mo(CN)_6]$ ($TMSO_2$), $K_2Mo(CN)_5$ ($TMSO_2$), $K_4[W(CN)_8]$ ($TMSO_2$), $K_4[W(CN)_6]$ ($TMSO_2$), $K_3[Mn(CN)_6]$ (DMF), $K_2Mn^{II}[Mn^{II}(CN)_6]$ ($TMSO_2$), $K_4[Fe(CN)_6]$ (DMF), $K_6[Co_2(CN)_{10}]$ (DMF), $K_3Co(CN)_5$ (DMF), $K_2[Ni(CN)_4]$ (DMF), and $K_4[Ni_2(CN)_6]$ (DMF).[24] The first three compounds were inert to nitrosyl chloride. The other results obtained are described below under the starting compounds as headings.

Results and Discussion

$K_4[Mo(CN)_8]$.—The pale yellow material isolated (yield 55–65%) proved to be the octacyanomolybdate(V). *Anal.* Calcd for $K_3[Mo(CN)_8]$: K, 27.84; Mo, 22.77; CN, 49.39. Found: K, 28.09 ± 0.28; Mo, 22.56 ± 0.01; CN, 48.5 ± 0.5 (sodium fusion). The infrared spectrum showed absorption bands at 2147 (s, sp) and 2135 cm^{-1} (vs, sp), in contrast to $K_4[Mo(CN)_8]$ which gave bands at 2135 (m, sp), 2129 (m, sp), 2123 (s, sp), and 2104 cm^{-1} (vs, sp). The gram-susceptibility of the substance was found to be $(3.20 \pm 0.08) \times 10^{-6}$ cgsu, corresponding to an effective magnetic moment of 1.92 BM and showing, as expected, the presence of one unpaired electron.

$K_4[Mo(CN)_6]$.—Analytical data for the brown product (yield 65–70%) showed it to be the corresponding molybdenum(III) complex. *Anal.* Calcd for $K_3[Mo(CN)_6]$: K, 31.76; Mo, 25.98; N, 22.75. Found: K, 29.91 ± 0.36; Mo, 25.27 ± 0.03; N, 22.47 ± 0.11 (modified Kjeldahl). The infrared spectrum of the product exhibited bands at 2104 (vs, br) and 2045 cm^{-1} (w) (starting compound: principal bands at 2055, 2010, 1960 cm^{-1}). The effective magnetic moment of the material was 1.24 BM.

$K_2Mo(CN)_5$.—A most interesting compound was found when potassium pentacyanomolybdate(III) was treated with nitrosyl chloride. On the basis of the analytical data, the olive-colored product (yield 55–65%) had the empirical formula $K_{1.5}Mo(CN)_5$. *Anal.* Calcd for $K_{1.5}Mo(CN)_5$: K, 20.60; Mo, 33.24; N, 24.30. Found: K, 21.15 ± 0.18; Mo, 33.49 ± 0.05; N, 23.9 ± 0.01 (modified Kjeldahl). The infrared spectrum had absorption bands at 2160 (vs) and 2122 cm^{-1} (s) in the cyano region, as well as bands at 3300 (w, br), 1605 (w, br), and 1550 cm^{-1} (w), the latter bands probably being due to adsorbed methanol or water. The starting complex exhibited principal bands at 2130 (s), 2120 (vs), and 2110 cm^{-1} (s), in excellent agreement with the literature values.[5] The formulation of the product as a complex containing both Mo(III) and Mo(IV), $K_3Mo^{III}Mo^{IV}(CN)_{10}$, is consistent with both the analytical and spectral data. On the assumption that no change in coordination number of molybdenum occurs when potassium pentacyanomolybdate reacts with nitrosyl chloride, the shift to higher frequency for cyano absorption correlates with an increase in oxidation state of the metal.[25] In terms of the formula proposed, the magnetic moment of the material was found to be 1.41 BM, indicating the presence of one unpaired electron.

$K_4[W(CN)_8]$.—Potassium octacyanotungstate(IV) exhibited behavior analogous to that of the corresponding molybdenum compound. The yellow product (yield *ca.* 65%) obtained was the tungsten(V) complex. *Anal.* Calcd for $K_3[W(CN)_8]$: K, 23.03; W, 36.10; CN, 40.87. Found: K, 23.08 ± 0.02; W, 36.15 ± 0.10; CN, 40.7 ± 0.3 (sodium fusion). The infrared spectrum exhibited bands at 2154 (s, sp), 2147 (vs, sp), and 2136 cm^{-1} (m, sp), whereas the bands for the tungsten(IV) complex were at 2137 (m, sp), 2126 (s, sp), 2123 (s, sp), and 2094 cm^{-1} (vs, sp). The gram-susceptibility for the tungsten(V) product was $2.37 \pm 0.17 \times 10^{-6}$ cgsu; the effective magnetic moment was 1.84 BM.

The oxidation of the octacyanometal(IV) complexes by nitrosyl chloride offers a superior method for the preparation of the corresponding molybdenum(V) and tungsten(V) compounds. Not only are the yields good but the procedure is extremely simple. Previous investigators[26–29] have obtained these substances by chemical or electrolytic oxidation of aqueous solutions of the metal(IV) complexes, isolating the desired compounds as their insoluble silver salts and converting the latter to potassium salts.

$K_4[W(CN)_6]$.—Analytical data for the dark brown product (yield 60–65%) showed it to be primarily $K_2[W(CN)_5H_2O]$ contaminated with some impurity. *Anal.* Calcd for $K_2[W(CN)_5H_2O]$: K, 19.06; W, 44.82; C, 14.64; N, 17.08; H, 0.49. Found: K, 18.02 ± 0.24; W, 42.14 ± 0.59; C, 14.09 ± 0.00; N, 15.67 ± 0.08; H, 0.45 ± 0.00 (C, H, and N determined by combustion); K:W ratio, 2.00:1.00. The infrared spectrum of the brown material showed bands at 2104 (s, br) and 2150 cm^{-1} (s, br) in the cyano region as well as water absorptions at 3400 (w, br) and 1610 cm^{-1} (m), whereas the starting complex gave strong bands at 2080, 2010, and 1950 cm^{-1}. The gram-susceptibility of the product was $(0.60 \pm 0.30) \times 10^{-6}$ cgsu, corresponding to an effective magnetic moment of 1.18 BM (compare with that for $K_3[Mo(CN)_6]$). It is likely that the water in the product was absorbed from the methanol used as an extractive agent.

$K_3[Mn(CN)_6]$.—This substance was oxidized to a canary yellow material (yield 80–85%) which proved to be the corresponding manganese(IV) complex. *Anal.* Calcd for $K_2[Mn(CN)_6]$: K, 27.04; Mn, 18.99; C, 24.91; N, 29.06. Found: K, 26.31 ± 0.17; Mn, 18.91 ± 0.03; C, 24.01; N, 27.76 (carbon and nitrogen determined by combustion); oxidation state of manganese, 3.89 ± 0.02. The infrared spectrum of

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(24) Specific details for the individual reactions, including the isolation and treatment of products, may be found in the Ph.D. thesis of J. R. Fowler, University of Kansas, 1969. A microform of the thesis is available at University Microfilms, Ann Arbor, Mich. 48106.

(25) M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

(26) O. Collenberg and B. Anderson, *Z. Elektrochem.*, **31**, 558 (1925).

(27) O. Olsson, *Ber.*, **47**, 917 (1914).

(28) W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927).

(29) H. H. Willard and R. C. Thielke, *J. Am. Chem. Soc.*, **57**, 2609 (1935).

the compound exhibited bands at 2240 (vs) and 2150 cm^{-1} (s, sp) while the starting complex showed a single absorption band at 2115 cm^{-1} (vs, sp). The shift in the infrared absorption to higher frequencies is consistent with oxidation of the central metal atom with no change in coordination number.[25] The gram-susceptibility of the compound was found to be (23.3 ± 0.2) × 10^{-6} cgsu and the effective magnetic moment was 3.94 BM. The latter value is very close to the calculated "spin-only" moment expected for a complex in which the central metal atom has a d^3 configuration. The yellow complex undergoes immediate decomposition with the formation of manganese dioxide on treatment with deaerated water.

It is probable that $K_2[Mn(CN)_6]$ represents the first manganese(IV)–cyano complex unequivocally characterized. Yakamich reported[30] the preparation of $K_4[Mn(CN)_8]$ by reaction between potassium permanganate and potassium cyanide in alkaline solution, but Goldenberg[31] was unable to reproduce the synthesis. He reported that the product of reaction was a cyano complex of manganese(III) contaminated with potassium hydroxide.

$K_2Mn^{II}[Mn^{II}(CN)_6]$.—Reaction between this complex and nitrosyl chloride in $TMSO_2$ yielded a tan solvent-insoluble substance and a small amount of a yellow soluble material which was characterized as potassium hexacyanomanganate(IV). Chemical analysis of the tan product (yield 65–80%) showed it to have the empirical formula $KMn_2(CN)_6$. *Anal.* Calcd for $KMn_2(CN)_6$: K, 12.82; Mn, 36.01; CN, 51.17. Found: K, 12.63 ± 0.03; Mn, 36.13 ± 0.08; CN, 48.72 ± 0.5 (method of Williams). On the basis of the analysis, the product was formulated as an Mn(II)–Mn(III) complex, $KMn^{II}[Mn^{III}(CN)_6]$. The infrared spectrum exhibited a single absorption band at 2147 cm^{-1} (vs, sp), while that of the starting material had bands at 2115 (w), 2125 (w), and 2060 cm^{-1} (vs). The shift to higher frequency in the product is consistent with oxidation of the central metal atom with no change in coordination number. (The weak bands at 2115 and 2125 cm^{-1} are attributed to the presence of a small amount of $K_3[Mn(CN)_6]$. In a previous investigation from this laboratory,[5] it was reported that a single absorption band at 2060 cm^{-1} was found for $K_2Mn^{II}[Mn^{II}(CN)_6]$ and that $K_3[Mn^{III}(CN)_6]$ showed three absorptions—2117, 2126, and 2148 cm^{-1}—rather than only the one found at 2115 cm^{-1} in this investigation.) The gram-susceptibility of the tan substance was (47.25 ± 0.25) × 10^{-6} cgsu. This value leads to an "average" magnetic moment of 4.19 BM for each manganese atom in the compound. This amount lies between the spin-only value expected for high-spin manganese(II) (five unpaired electrons) and low-spin manganese(III) (two unpaired electrons) and thus is also consistent with our formulation. Our product would appear to be identical with that isolated by Brown and Shriver[32] from the reaction between potassium hexacyanomanganate(III) and manganese(II) acetate in aqueous solution and assigned the formula $KMn^{II}[Mn^{III}(CN)_6]$. Although no analytical or magnetic data were given, the tan material these investigators obtained exhibited a single infrared absorption band at 2151 cm^{-1} in the cyano region. X-Ray powder data yielded a face-centered cubic lattice parameter of 10.63 Å, consistent with the cyano-bridged type structure of Prussian blue.

$K_4[Fe(CN)_6]$.—The only product isolated from reaction of this compound with nitrosyl chloride was shown by its infrared spectrum to be potassium hexacyanoferrate(III).

$K_6[Co_2(CN)_{10}]$ and $K_3Co(CN)_5$.—The binuclear complex yielded as products a yellow-green DMF-insoluble material and a yellow soluble substance. The insoluble product gave the following analytical data: (1) K, 23.05 ± 0.16; Co, 23.32 ± 0.12; C, 20.50 ± 0.02 (combustion); N, 24.02 ± 0.04 (combustion); H, 0.86 ± 0.12 (combustion); empirical formula, $K_{1.56}Co(CN)_{4.53}(H_2O)_{1.12}$; (2) K, 26.77 ± 0.07; Co, 22.02 ± 0.13; C, 20.28; N, 23.33; H, 0.54; empirical formula, $K_{1.83}Co(CN)_{4.49}(H_2O)_{0.72}$; (3) K, 25.96 ± 0.09; Co, 22.41 ± 0.03; C, 20.91 ± 0.13; N, 23.95 ± 0.00; H, 0.76 ± 0.09; empirical formula, $K_{1.75}Co(CN)_{4.54}(H_2O)_{0.99}$ (water content calculated from the hydrogen analysis) (yield, 1.5–1.8 g from 3.0 g of starting materials). Although the analytical data indicate that the product is not a single compound, they do show that most of the cobalt has been converted to the tripositive state. The infrared spectrum of the product (obtained *after extraction* with methanol) in each preparation had absorption bands in the cyano region at 2193 (s) and 2131 cm^{-1} (vs, sp) and additional bands at 3300 (m, br) and 1610 cm^{-1} (m). The cyano bands were also present prior to the extractive process; in addition, bands characteristic of DMF were observed, but no water bands.

The yellow DMF-soluble product (0.3–0.5-g yield) exhibited, just after isolation, a single cyano band at 2145 cm^{-1} (s, br) as well as bands due to the solvents employed in its preparation and separation. However, after the material was dried *in vacuo*, the band at 2145 cm^{-1} was no longer present but new cyano bands appeared at 2190 (m) and 2130 cm^{-1} (s). (*Cf.* the spectrum of the DMF-insoluble material.) Since the spectrum also showed the presence of DMF, complete analytical data of the product were not obtained. However, analysis of products obtained from two separate experiments yielded K:Co ratios of 1.94:1.00 and 1.87:1.00, respectively.

No change in the nature of the reaction was observed when the monomeric complex $K_3Co(CN)_5$ was substituted for the binuclear species.

There is little doubt that the DMF-insoluble and -soluble products are mainly polynuclear and mononuclear forms, respectively, of the same cobalt(III) species, $K_2[Co(CN)_5H_2O]$. Thus, the infrared spectrum of $K_2[Co(CN)_5H_2O]$[33] exhibits a single band at 2140 cm^{-1} compared to the single band at 2145 cm^{-1} for the soluble

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(30) A. Yakamich, *Compt. Rend.*, **190**, 681 (1930).

(31) N. Goldenberg, *Trans. Faraday Soc.*, **37**, 847 (1940).

(32) D. B. Brown and D. F. Shriver, *Inorg. Chem.*, **8**, 37 (1969).

(33) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 166.

product. The sodium complex $Na_2[Co(CN)_5H_2O]$ undergoes spontaneous polymerization in aqueous solution and in the solid state[34] and the infrared spectrum of the polymer shows bands at 2202 (m) and 2135 cm^{-1} (s),[35] very similar to the cyano bands for the DMF-insoluble product and also for the soluble product after drying *in vacuo*. When dehydrated the sodium salt shown above changes from yellow to green, a property also possessed by both products obtained in this work.

$K_2[Ni(CN)_4]$ and $K_4[Ni_2(CN)_6]$.—The green precipitate formed in each case on reaction with nitrosyl chloride was identified as $Ni(CN)_2 \cdot x$DMF by means of infrared spectroscopy. The spectrum of the material obtained from the nickel(II) complex showed cyano bands at 2170 (vs, sp) and 2129 cm^{-1} (w), as well as bands characteristic of DMF. For the product isolated from the nickel(I) complex, bands were found at 2166 (vs, sp) and 2132 cm^{-1} (w). The infrared spectrum of $Ni(CN)_2 \cdot 4H_2O$ (taken for comparison) exhibits absorption bands at 2166 (vs, sp) and 2130 cm^{-1} (w) in the cyano region, as well as bands attributable to water at 3710, 3500, and 1620 cm^{-1}.

The $K_2[Ni(CN)_4]$–NOCl system is the only one in which reaction occurs and it is not the metal which is oxidized by the nitrosyl chloride. It would appear that oxidation of the cyanide ligand takes place. This hypothesis is supported by electrochemical data[24] obtained for the tetracyanonickelate(II) complex. Polarography at a rotating platinum electrode in DMF with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte showed that oxidation of the complex occurred at $E_{1/2}$ (*vs.* sce) = +0.89 V. Cyclic voltammetry at a stationary platinum electrode indicated that the oxidation wave obtained from polarography was irreversible and corresponded to a two-electron change. Oxidation of cyanide ion to cyanogen would account for the electrochemical information.

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Pressure-Jump Relaxation Kinetics of Magnesium(II), Manganese(II), Nickel(II), Cobalt(II), Copper(II), and Zinc(II) *m*-Benzenedisulfonates in Anhydrous Methanol at 25°

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The kinetics of ion association of the *m*-benzenedisulfonates of Mg^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} have been studied by the pressure-jump relaxation technique. Through the support of results by electrical conductance these data have been interpreted by the Eigen multistep theory of ionic association. The observed relaxation times are interpreted as due to the process of penetration of the inner sphere of the metals by the ligand, this process being coupled to a much faster outer-sphere equilibration. The rates of complexation were found to be much slower than the nmr rates of solvent exchange. This is discussed in terms of alternate mechanisms.

Introduction

Relaxation kinetics, nmr kinetics, and other more conventional tools like thermodynamics and mass transport, when applied to the process of complexation and ligand exchanges, have given a rather complete picture of the dynamics of short-range interactions in dilute aqueous ionic solutions.[2]

In particular for divalent transition metal ions the process of ionic association and complexation appears to be multistep[3] starting from a diffusion-controlled approach between solvated ions to form an outer-sphere ion pair. Whether this diffusion process is always a single discrete one as in the original Von Smoluchowsky–Debye[4a] and Eigen[4b] calculations or sometimes characterized by a spectrum of relaxation times due to the many possible configurations of the outer-sphere complexes (as possibly suggested by recent ultrasonic measurements by Plass and Kehl[5] on metal sulfates) remains to be established.

In any case this diffusion-controlled process is followed by a slower cation desolvation with the ligand entering the first coordination sphere of the metal. The mechanism[6] of this process differs depending on the metal and the ligand, varying from the limits of an association type (with the formation of a seven-

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(1) This work is part of the thesis of G. Macri in partial fulfillment for the requirements of the degree of Doctor in Philosophy, Polytechnic Institute of Brooklyn, 1970.

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