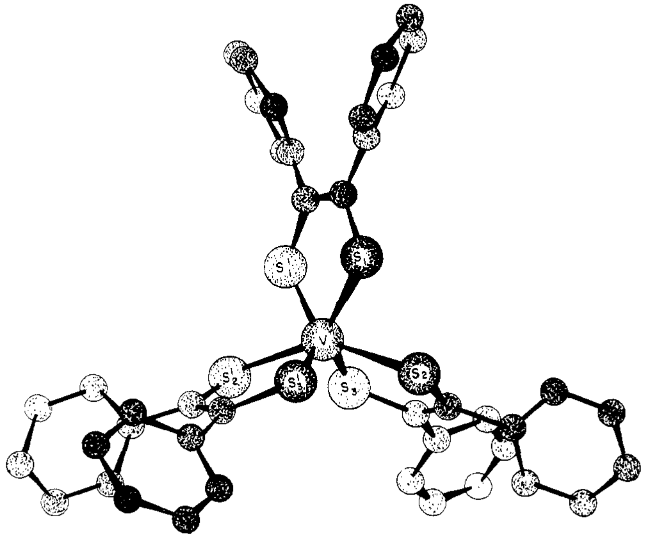

Figure 1.—A perspective drawing of an isolated molecule of the $V(S_2C_2(C_6H_5)_2)_3$ complex. Phenyl hydrogens are not shown.

$M(S_2C_2R_2)_3$ systems, such that we have $4e' < 3a_1' < 2a_2' < 5e' < 4e''$. The proposed ground state for $V(S_2C_2(C_6H_5)_2$ is therefore . . . $(4e')^4(3a_1')^1 = {}^2A_1$.[31] This means that if the 4e′ level is assigned to the ligand (as is traditional), the complex is formally a d^1 complex of V(IV) and $[(S_2C_2(C_6H_5)_2)_3{}^{4-}]$ and the ligand system is fully oxidized by two electrons from its classical trisdithiolate state. A second, equally arbitrary formalism for the complex may be derived by assigning the filled 4e′ level to the metal. In this formulation $V(S_2C_2(C_6H_5)_2)_3$ is a d^5 V(0) complex with an uncharged $[(S_2C_2(C_6H_5)_2)_3]$ ligand unit. Although the V(IV)–$[L_3{}^{4-}]$ formulation may seem more appealing in view of the average C–C distance of 1.41 A, the average C–S distance of 1.69 A suggests C═S and thus is more compatible with a V(0) $[L_3]$ model. However, in either case it is clear that the ligand system is at least partially oxidized and the 4e′ level is strongly delocalized over the MS_2C_2 chelate ring.

It is also worth noting that the assignment of the unpaired electron to $3a_1'$ $(s + z^2)$ is not in conflict with the esr data which show a nearly isotropic g value of 1.99 and a substantial isotropic ^{51}V hyperfine splitting of 61.6 gauss.[8b,8c] In this respect the proposed electronic structure is superior to . . . $(4e')^4(2a_2')^1 = {}^2A_2'$, in which the unpaired electron would be entirely out on the ligands. In any event, further studies are needed to help elucidate the electronic structures of the first-row systems.[31,32]

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation. We wish to thank Mr. Zvi Dori and Mr. Edward Stiefel for their timely remarks in discussion, and Mr. Sam La Placa of Brookhaven National Laboratory for his helpful advice in matters relating to the solution of the structure.

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(31) According to the Schrauzer–Mayweg scheme, the ground state for the undistorted $V(S_2C_2(C_6H_5)_2)_3$ complex should be $^2E'$. If this assignment is correct, the observed distortions in the coordination geometry can be accommodated from Jahn–Teller considerations. However, it is on the strength of the available solution esr data that we suggest the $^2A_1'$ ground state, as discussed in the text. More detailed studies including a single crystal esr investigation of the $V(S_2C_2(C_6H_5)_2)_3$ complex doped into the isomorphous $Cr(S_2C_2(C_6H_5)_2)_3$ complex and the calculation of spin Hamiltonian parameters appear necessary in order to establish firmly the ground-state configuration of $V(S_2C_2(C_6H_5)_2)_3$.

(32) In a preliminary communication of their work on the trisdithioglyoxa complexes [G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Chem. Ind.* (London), 1464 (1965)], Schrauzer, *et al.*, suggested the energy level ordering $4e' < 3a_1' < 2a_2' < 5e'$ for the neutral third row complex $Re(S_2C_2H_2)_3$. This ordering agrees qualitatively with our proposed energy-level scheme for the first-row $V(S_2C_2(C_6H_5)_2)_3$ complex. However, Schrauzer and Wayweg[25] now suggest $^2E'$ ground states for the neutral V and Re complexes on the basis of their subsequent calculations.

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Reactions of Potassium Hexacyanochromate(III) and Some Transition Metal Cyanonitrosyls with Molecular Hydrogen at Elevated Temperatures

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The reactions of potassium hexacyanochromate(III) and a number of pentacyanonitrosyl complexes with molecular hydrogen at moderately elevated temperatures have been investigated. At 400°, potassium hexacyanochromate(III) is reduced to a compound of the empirical formula $K_3Cr(CN)_4$. The same substance is formed when potassium pentacyanonitrosylchromate(I) is treated with hydrogen at the same temperature. Reaction of hydrogen and potassium pentacyanonitrosylferrate(II) monohydrate at 230° yields a substance of the composition $K_2Fe(CN)_4$. From the interaction of potassium pentacyanonitrosylmanganate(I) with hydrogen at 330° there is isolated a material of the approximate composition $Mn(CN)_{2.1}$. At 200°, potassium pentacyanonitrosylvanadate(−I) monohydrate is converted by hydrogen to a compound corresponding to the composition $K_5V(CN)_5$. Infrared spectra and magnetic moments indicate the presence of bridging cyanide groups in all of the products. All but the vanadium-containing product are water insoluble.

In a previous report from our laboratory[1] the reduction of some transition metal cyano complexes by molecular hydrogen at moderately elevated temperatures was described. This technique yielded, by removal of one or two cyanide ligands as hydrogen cyanide, complexes containing the transition metals in low oxidation states. The current paper extends the previous

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

work. Specifically, the reaction of the following compounds with hydrogen was studied: potassium hexacyanochromate(III); potassium pentacyanonitrosylchromate(I), $K_3Cr(CN)_5NO$; potassium pentacyanonitrosylferrate(II) monohydrate, $K_2Fe(CN)_5NO\cdot H_2O$; potassium pentacyanonitrosylmanganate(I), $K_3Mn(CN)_5NO$; and potassium pentacyanonitrosylvanadate(−I) monohydrate, $K_5V(CN)_5NO\cdot H_2O$. The pentacyanonitrosyl complexes were chosen for investigation since it was believed that the nitrosyl group might be more easily removed than a cyanide ligand, leaving unsymmetrical cyano complexes which might then be readily reduced.

For the pentacyanonitrosyl complexes listed above, the oxidation state of the central atom is assigned on the basis that the nitrosyl ligand coordinates as the NO^+ ion. Coordination of the ligand as the cation in these complexes has been deduced from infrared data.[2,3] It should be stated, however, that there is still considerable question concerning the actual nature of the metal–NO bond in these compounds.

Experimental Section

Materials.—Hydrogen and nitrogen were used directly from commercial cylinders; there was never any indication of adverse effects attributable to oxygen or moisture in the gases. The procedure for the preparation of potassium hexacyanochromate(III) was essentially that outlined by Bigelow,[4] except that chromium(III) acetate, now commercially available, was used directly. A modification of the method of Griffith, Lewis, and Wilkinson[5] was employed to prepare potassium pentacyanonitrosylchromate(I); in this modification potassium chromate rather than chromium(VI) oxide was used as a starting material.[6] Potassium pentacyanonitrosylferrate(II) monohydrate was obtained by the method described by Greene and Chamberlain[7] for the preparation of the dihydrate; our product was dried at 100° *in vacuo* rather than at 30°. The procedure of Cotton, *et al.*,[8] was used for the synthesis of potassium pentacyanonitrosylmanganate(I). Potassium pentacyanonitrosylvanadate(−I) monohydrate was synthesized according to the procedure of Griffith, Lewis, and Wilkinson.[3] Potassium and transition metal contents were determined in each compound and all analyses were quite satisfactory.

Analytical Methods.—Potassium was determined gravimetrically from acidic solution as the tetraphenylborate.[9] Chromium was first oxidized to dichromate by a hot mixture of 70% perchloric and concentrated sulfuric acids and then determined iodometrically. Iron was determined volumetrically according to a standard procedure.[10] Manganese was determined in the following manner. The sample was first oxidized by boiling with sodium bismuthate in nitric acid solution, and then the manganese was reduced to the dipositive state by sulfurous acid. The solution was boiled, cooled, diluted with nitric acid, and oxidized in the cold with an excess of bismuthate. After filtration, the permanganate formed was reduced by an excess of standard ferrous ammonium sulfate solution in the presence of phosphoric acid. Unreacted iron(II) was then titrated with standard potassium permanganate solution. Fot the analysis of vanadium, the sample was dissolved in water; the vanadium was converted to the pentapositive state by oxidation with potassium permanganate in acid solution and then reduced to the tetrapositive condition by means of sodium bisulfite. After removal of excess sulfur dioxide by boiling, vanadium(IV) was titrated with standard potassium permanganate solution.

Cyanide analysis is reported for only one of the products, that obtained from $K_3Mn(CN)_5NO$ and the only one which did not contain potassium. In this case, a weighed sample of the product was slowly heated with an excess of potassium bisulfate to the latter's melting point (210°) and then the heating was gradually continued until all of the product had dissolved. (If the fusion is carried out correctly, the cyanide is converted to ammonium ion.) Following the fusion process, the melt was allowed to cool, dissolved in water, and treated with 50% sodium hydroxide solution in a Kjeldahl flask. Ammonia was then distilled into a 4% boric acid solution and titrated to a pH of 4.50 with standard hydrochloric acid. It should be pointed out that none of the various methods reported in the literature for the determination of cyanide proved to be satisfactory for our products, all of which apparently contained bridged cyanide groups. The molecular formulas of the products (excepting that from the manganese system) were deduced from potassium and transition metal values only. In all instances, it was established by chemical and infrared methods that no starting material remained, that no nitrosyl group was present, and that the products contained cyanide.

Infrared Spectra.—A Perkin-Elmer Model 421 grating spectrophotometer was employed for these measurements. For the preliminary thermal decomposition experiments (to be described later), volatile products obtained in the vacuum line were transferred to 10-cm sodium chloride plate gas cells for infrared analysis. Identification was made in each case by comparison with a spectrum of a pure substance or by reference to a published compilation of gas-phase spectra.[11] Spectra of solids were determined in either Nujol or Fluorolube mulls.

Magnetic Susceptibility Measurements.—These measurements were made by the Gouy method. The accuracy and reproducibility of the balance was checked by determining the susceptibility of $Hg[Co(SCN)_4]$ against water as the standard. The measurements were made at room temperature, *ca.* 25°, and were taken at three field strengths for each sample.

Conductance Measurements.—Only one product, $K_5V(CN)_5$, was soluble in water and its molar conductance, as well as those of some well-known complexes, was measured at 25° in that medium. For this purpose, an Industrial Instruments Co. Model RC-16B2 bridge with two conventional dip-type cells was used. The cell constant was found by measuring the resistance of a 0.01 *M* potassium chloride solution, for which the specific conductivity is known to be 1.413×10^{-3} ohm^{-1} cm^{-1} at 25°. Solutions of the complexes measured were 10^{-3} *M* in concentration and were prepared using demineralized distilled water.

Apparatus for Reductions with Hydrogen.—The tube furnace, temperature control and measuring units, and rotating reaction tube were essentially those described previously.[1,12] A reaction chamber longer than 4–5 in. in the rotating tube proved to be unsatisfactory, owing to thermal gradients in the furnace.

General Outline of Experimental Procedures for Reactions.—Preliminary experiments were performed to establish the temperature at which thermal decomposition *in vacuo* was significant for each compound and to identify volatile decomposition products. A sample (2–5 g) of starting material was heated in a standard-taper test tube in a vacuum line at 10^{-4} mm until evidence of decomposition was noted, and the temperature was then

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[2] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

[3] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1632 (1959).

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

[5] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

[6] Detailed directions for the synthesis of the various cyanonitrosyl complexes and analytical methods employed may be found in the Ph.D. thesis of David F. Banks, University of Kansas, 1967.

[7] A. F. Greene, Jr., and M. M. Chamberlain, U. S. Department of Commerce, Office of Technical Services, AD 282 397, Washington, D. C., 1962.

[8] F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).

[9] K. Sporek and A. F. Williams, *Analyst*, **80**, 347 (1955).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 572.

[11] R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

[12] J. S. Yoo, Ph.D. Thesis, University of Kansas, 1964.

kept essentially constant for some time. The heating was effected with the use of either a silicone-oil bath or a small tube furnace, temperatures being measured with either a thermometer or a chromel–alumel thermocouple and a balancing potentiometer. Volatile products were condensed into one or more U-shaped bulbs, cooled by either liquid nitrogen or a Dry Ice–2-propanol bath; condensates were then transferred to sodium chloride gas cells for infrared analysis.[13]

To establish the maximum operating temperatures for carrying out reductions at atmospheric pressure, a sample (0.5–2 g) of starting compound was added to the reaction chamber of the rotating reaction tube and slowly heated in a stream of nitrogen. The temperature at which decomposition began was noted; this was generally 20–40° higher than the temperature at which decomposition occurred under vacuum. The temperatures found in these experiments were regarded as the *maximum* for the reduction of those compounds ($K_2Fe(CN)_5NO \cdot H_2O$ and $K_3Mn(CN)_5NO$) which evolved nitric oxide on thermal decomposition under vacuum. A second sample of each of those compounds ($K_3Cr(CN)_6$, $K_3Cr(CN)_5NO$, and $K_4V(CN)_5NO \cdot H_2O$) which did not evolve nitric oxide on decomposition was heated for several days in a stream of nitrogen at a temperature 10–20° below the decomposition temperature. In all cases, little or no cyanogen was formed. (This gas was determined, after removal of any traces of hydrogen cyanide in acidified silver nitrate solution, by absorption in aqueous sodium hydroxide and titration of cyanide ion formed with standard silver nitrate solution.) These experiments established the *maximum* temperatures at which the three compounds cited above could be reduced by molecular hydrogen without interference from thermal decomposition.

To identify gaseous products of reaction of the starting compounds with hydrogen, a sample of each was heated in the vacuum line under a hydrogen pressure of approximately 300 mm. The temperature was raised until volatile products were formed and these were collected for infrared analysis. It was observed that those compounds which did not evolve nitric oxide on thermal decomposition reacted with hydrogen at temperatures 20–300° below those where decomposition was significant.

Following the preliminary experiments described above, reaction between starting compound and molecular hydrogen was carried out in the following manner. The reaction chamber was about one-fourth filled with the sample (0.5–2.5 g) and the rotating reaction tube was assembled and placed in the furnace. Solutions appropriate for the absorption of gaseous products (*e.g.*, ferrous sulfate for nitric oxide, 4% boric acid for ammonia, and acidified silver nitrate for hydrogen cyanide) were placed in U-shaped traps connected to the reaction tube. Agitation of the sample was initiated by means of the rotating-tube assembly and the sample was slowly heated to 100° in a stream (20–50 ml/min) of nitrogen to remove bound and adsorbed water. The nitrogen was then replaced with a current of hydrogen, which was allowed to flow continuously at about 20 ml/min. The temperature was slowly raised to the previously determined operating level and was thereafter maintained at this level by the proportional controller. Reaction was permitted to proceed until volatile products were no longer evolved. When reaction was complete, the power was turned off and the furnace was allowed to cool. Rotation and gas flow were continued for at least 8 hr after the reaction tube had reached room temperature, so as to sweep all volatile products into the absorption traps. The solid product was transferred to a ground-joint weighing bottle for analysis. The silver cyanide in the silver nitrate trap was collected on a sintered-glass crucible, washed several times with distilled water, and dried to constant weight at 110°. The ammonia in the boric acid trap was determined by titration to pH 4.5 with standard hydrochloric acid solution. No attempt was made to estimate quantitatively the nitric oxide evolved, since much of it is swept from the ferrous sulfate solution by the hydrogen stream.

Reactions of Hydrogen with Starting Compounds. Specific Systems.—The reduction of potassium hexacyanochromate was effected at 400°, approximately 2 weeks being required for the reaction to go to completion. The solid product was olive-green, and ammonia and hydrogen cyanide were the gaseous products characterized and determined. There was no evidence for the formation of cyanogen. The solid product was analyzed for potassium and chromium. Reduction of potassium pentacyanonitrosylchromate(I) was also carried out at 400°. Complete reaction occurred in 1–2 weeks, the final product was identical in appearance with that obtained from potassium hexacyanochromate, and again the only gaseous products were ammonia and hydrogen cyanide.

Following removal of adsorbed water from potassium pentacyanonitrosylferrate(II) monohydrate at 100° in a stream of nitrogen, reduction with hydrogen was carried out at 230°. The first gas evolved was nitric oxide, its evolution being soon followed by that of hydrogen cyanide; no ammonia was observed. Reaction was complete in about 2 days and the solid product was tan. It was analyzed for potassium and iron.

Reduction of potassium pentacyanonitrosylmanganate(I) was completed in about 1 week at 330°. Gaseous products were nitric oxide, ammonia, and hydrogen cyanide. Examination of the brown solid product remaining showed that it was not a homogeneous single phase. The solid was transferred to a weighed sintered-glass crucible containing a Teflon-coated stirring bar, anhydrous methanol was added to the crucible in 10-ml portions, and the contents were stirred for 3–5 min and filtered. The extraction was repeated until the filtrate gave no test for cyanide ion and then the residue in the crucible was sucked dry, dried overnight *in vacuo*, and analyzed for manganese and cyanide. Analysis of the latter was carried out as described under the section on analytical methods. The methanol-soluble material was completely precipitated by pouring the solution into 10 volumes of ether, and the mixture was filtered. The precipitate was dried, weighed, and analyzed for potassium, strong base, and cyanide ion. (The last was determined by the Liebig method.)

Water was removed from potassium pentacyanonitrosylvanadate(−I) monohydrate at 100° in a stream of nitrogen. The product was then reduced in a stream of hydrogen at 200°. Ammonia and nitrous oxide were observed as volatile products and reaction was complete within 2 days. The pink solid remaining after reduction was analyzed for potassium and vanadium and its conductance in aqueous solution was measured.

Infrared spectra and magnetic measurements were obtained for all reduction products.

Results and Discussion

Some Observations on the Thermal Decomposition of Starting Materials.—Potassium hexacyanochromate(III) is thermally stable in a nitrogen atmosphere to approximately 450°; above this temperature decomposition begins to occur and cyanogen is liberated. No attempt was made to study the decomposition at temperatures much beyond 450°.

The potassium pentacyanonitrosyls studied fall into two classes on the basis of their thermolysis. For two of the compounds, the pentacyanonitrosylchromate(I) and the pentacyanonitrosylvanadate(−I), nitric oxide is not formed in thermal decomposition, whereas for the other two, the pentacyanonitrosylferrate(II) and the pentacyanomanganate(I), nitric oxide is the primary volatile product. Potassium pentacyanonitrosylchromate(I) begins to decompose very slowly at 400° and somewhat more rapidly at 450°; gaseous products include nitrogen, nitrous oxide, carbon dioxide, and cyanogen. The pentacyanonitrosylvanadate(−I)

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(13) In some instances, the condensates were subjected to mass spectrometric analysis.

monohydrate loses the bound water, but is otherwise stable below 400°. Decomposition is quite slow at 550°, and at 580° the compound blackens and finally sinters. Gaseous products are nitrogen, nitrous oxide, and carbon dioxide. Potassium pentacyanonitrosylferrate(II) monohydrate, a red-brown solid, decomposes rapidly at 230° at atmospheric pressure with the liberation of nitric oxide, leaving a blue solid. At about 250°, the latter becomes light brown and cyanogen is liberated. Potassium pentacyanonitrosylmanganate(I) undergoes rapid decomposition at 330° under atmospheric pressure, with nitric oxide being the primary volatile product. Smaller amounts of nitrous oxide, nitrogen, and cyanogen are also formed.[14]

There is an interesting parallel between the manner of thermal decomposition of the pentacyanonitrosyls and the N–O bond strengths in the complexes as inferred from infrared data. The N–O stretching frequencies for the complexes $K_5V(CN)_5NO$, $K_3Cr(CN)_5NO$, $K_3Mn(CN)_5NO$, and $K_2Fe(CN)_5NO$ are, respectively, 1575,[3] 1645,[5] 1730,[8] and 1945[8] cm^{-1}. Thus, the two compounds with the strongest N–O bonds lose nitric oxide primarily at the temperature where decomposition begins, whereas the other two, with weaker N–O bonds, decompose in a nonspecific manner which evidently involves bond rupture.

Potassium Hexacyanochromate(III) and Hydrogen.—Ammonia and hydrogen cyanide are the only volatile products of reaction at 400° and the source of these substances must obviously be cyanide ligand.[15] The proportion of the two gases varied from experiment to experiment, but the sum, expressed as recovered nitrogen, was relatively constant, 8.89 ± 0.45% (four experiments), and corresponded closely to that required (8.61%) for the loss of two cyanide ligands from the starting material.

The olive-green solid remaining after the reduction of potassium hexacyanochromate(III) has an empirical formula of $K_3Cr(CN)_4$. *Anal.* Calcd for $K_3Cr(CN)_4$: K, 42.90; Cr, 19.03. Found: K, 43.39 ± 0.77; Cr, 19.06 ± 0.23. The compound is insoluble in water and common organic solvents and is unaffected by boiling concentrated hydrochloric, nitric, or sulfuric acid, or their mixtures. It is slowly digested by hot saturated calcium hypochlorite solution and is oxidized to chromate ion by fusion with sodium peroxide and to dichromate ion by a fuming 1:1 mixture of 96% sulfuric and 70% perchloric acids.

The infrared mull spectrum of the compound (Table I) shows two sharp peaks in the C–N stretching region—one at 2178 cm^{-1} and the other at 2077 cm^{-1}. Since the starting material, $K_3Cr(CN)_6$, exhibits a single sharp band at 2130 cm^{-1}, the band at 2178 cm^{-1} is probably due to a bridging cyanide stretch.[16] The band at 2077 cm^{-1} can be interpreted in terms of an increase in the ratio of coordination number to oxidation number in going from $K_3Cr(CN)_6$ to $K_3Cr(CN)_4$.[17] (It is assumed that through cyanide bridging the coordination number of chromium in $K_3Cr(CN)_4$ is 6.)

TABLE I

MAGNETIC MOMENTS AND INFRARED ABSORPTION

Compound	μ_{eff}[a]	Infrared peaks
$K_3Cr(CN)_4$ (from $K_3Cr(CN)_6$)	2.52 ± 0.01	2178 s, 2077 s
$K_3Cr(CN)_4$ (from $K_3Cr(CN)_5NO$)	2.57 ± 0.19	2178 s, 2077 s
$K_2Fe(CN)_4$	3.97	2072 s, 2045 s
$Mn(CN)_{2.1}$	4.23 ± 0.11	2140 b
$K_5V(CN)_5$	Diamagnetic	2175 s, 2078 s, 2030 m

[a] The following comment regarding the significance of the magnetic moments has been made by a referee: "The magnetic moment is not proportional to the magnetic susceptibility. Therefore, it is not possible to calculate a physically meaningful magnetic moment from the nominal chemical formula for a compound which contains metal ions in different spin states. It is likely that two or more different spin states are present in some of these complexes and therefore the "magnetic moments" given are of qualitative significance but they do not represent true magnetic moments."

The effective magnetic moment of $K_3Cr(CN)_4$ is about 2.52 BM (Table I). This moment lies between the spin-only values expected for low-spin (one unpaired electron) and high-spin (five unpaired electrons) octahedral chromium(I) complexes and is consistent with the presence of bridging cyanide groups in the complex.[18] It has been shown that the ligand field strength of the nitrogen end of cyanide in some cubic cyanide-containing polymeric complexes lies below that for ammonia in the spectrochemical series.[19]

Potassium Pentacyanonitrosylchromate(I) and Hydrogen.—In this case, as with the hexacyanochromate(III), ammonia and hydrogen cyanide are the only volatile products of reduction. The quantity of hydrogen cyanide evolved was always less than that corresponding to the removal of one cyanide ligand. However, the sum of the amounts of ammonia and hydrogen cyanide, expressed as recovered nitrogen, agrees reasonably well with that expected from the loss of the nitric oxide ligand and one cyanide. *Anal.* Calcd for recovered nitrogen: 8.51. Found: 8.89 ± 0.54 (three experiments).

The solid product is identical in appearance, chemical properties, and analysis with that obtained from the hexacyanochromate. *Anal.* Calcd for $K_3Cr(CN)_4$: K, 42.90; Cr, 19.03. Found: K, 42.64 ± 0.28; Cr, 19.14 ± 0.15. See also Table I.

Potassium Pentacyanonitrosylferrate(II) Monohydrate and Hydrogen.—Reaction at 230° yields a light brown solid and nitric oxide and hydrogen cyanide as the volatile products. The amount of hydrogen cyanide liberated, determined as silver cyanide, corresponds substantially to that expected for the loss of one cyanide ligand. *Anal.* Calcd for liberated hydro-

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(14) Our results on the thermal decomposition of pentacyanonitrosyl complexes are to be compared with those reported by Greene and Chamberlain.[7]

(15) The ammonia doubtlessly is formed by the reduction of hydrogen cyanide, a reaction which we believe is catalyzed by either the starting complex or its reduction product $K_3Cr(CN)_4$.

(16) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(17) M. F. A. El-Sayed and R. K. Sheline, *ibid.*, **6**, 187 (1958).

(18) See footnote to Table I.

(19) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

gen cyanide: 8.33. Found: 8.47 ± 0.08 (three experiments). Moreover, the total weight loss of starting material agrees extremely well with that expected for the loss of the nitric oxide and cyanide ligands. *Anal.* Calcd weight loss: 23.7%. Found: 23.7 ± 0.2%.

The light brown solid has the empirical formula $K_2Fe(CN)_4$. *Anal.* Calcd for $K_2Fe(CN)_4$: K, 32.84; Fe, 23.46. Found: K, 32.64 ± 0.10; Fe, 23.39 ± 0.33. The product would appear to be analogous to the chamois-colored substance, $Na_2Fe(CN)_4$, obtained by Etard and Bemont from the thermal decomposition of $Na_2Fe(CN)_5NO \cdot 2H_2O$ *in vacuo* at 440°.[20] The material is unaffected by deoxygenated water but is converted to Prussian blue in contact with the air-saturated solvent. It is similarly oxidized without dissolution by hot concentrated sulfuric acid. Rapid and complete oxidation to ferrate(VI) ion, FeO_4^{2-}, occurs when the compound is heated with saturated calcium hypochlorite solution.

The infrared spectrum of the compound (Table I) contains two sharp peaks in the C–N region, one at 2072 cm^{-1} and the other at 2045 cm^{-1}. The starting material exhibits, under low resolution, a single C–N band at 2140 cm^{-1}. By comparison, the C–N stretching frequency in $K_4Fe(CN)_6$ is a sharp single peak at 2044 cm^{-1},[21] and that in Prussian blue is a broad band at 2075 cm^{-1}.[22] It would therefore seem likely that $K_2Fe(CN)_4$ contains both bridging and terminal cyanides, with the higher band being due to bridging C–N stretch and the lower to terminal C–N stretch.

$K_2Fe(CN)_4$ has an effective magnetic moment of 3.97 BM (Table I). This moment lies between the spin-only value expected for low-spin (no unpaired electrons) and high-spin (four unpaired electrons) octahedral iron(II) complexes. The magnetic moment for the complex thus is also indicative of the presence of bridging cyanide ligands.

Potassium Pentacyanonitrosylmanganate(I) and Hydrogen.—Reaction at 330° is accompanied by the evolution of nitric oxide, ammonia, and hydrogen cyanide. The quantities of the latter two gases varied from experiment to experiment; in five experiments the ammonia liberated varied from about 0.10 to 0.47 mole/mole of starting material and hydrogen cyanide varied from 0.43 to 0.75 mole. No pattern could be observed from the data.

The light brown solid remaining after completion of reaction proved to be a mixture containing appreciable quantities of potassium cyanide and potassium hydroxide. Extraction of the brown solid with cold methanol removed 63–64% of the material, leaving a dark brown residue. This residue was insoluble in water and common organic solvents, was unaffected by boiling hydrochloric, nitric, and sulfuric acids or their mixtures, but was rapidly oxidized to permanganate by bismuthate ion in boiling 1:3 nitric acid.

Analysis of the methanol extract showed the presence of potassium, cyanide, and hydroxide in the ratio of about 3:2:1. Presumably the potassium hydroxide arises in the following fashion. Part of the nitric oxide evolved is catalytically reduced by hydrogen with the formation of ammonia and water vapor, and the latter causes some hydrolysis of potassium cyanide produced on decomposition of starting material.

The dark brown material insoluble in methanol contains no potassium and gives no indication of the presence of bound nitric oxide according to its infrared spectrum. Analysis for manganese and cyanide gave the following results: Mn, 48.48 ± 0.69; CN, 48.23 ± 0.72 (five experiments); CN:Mn, (2.10 ± 0.06):1. The substance thus appears to be primarily manganese(II) cyanide and probably contains some manganese(III). In view of the difficulty in analyzing for cyanide in our products and the fact that analysis accounted for 96–98% of the material, it is likely that the CN:Mn ratio is actually a little greater than the 2.1:1 value obtained.

The infrared spectrum of the product exhibits a broad single peak at 2140 cm^{-1}. The starting compound gives a spectrum with bands at 2060 and 2100 cm^{-1} in the C–N stretching region and at 1725 cm^{-1} in the N–O region, and $K_4Mn(CN)_6$ which has only terminal cyanides exhibits a single band at 2060 cm^{-1}. The 2140-cm^{-1} band is thus in the range expected for a bridging cyanide stretching frequency; there would appear to be no significant fraction of unbridged cyanide groups in the material.

The effective spin-only magnetic moment calculated using the empirical formula $Mn(CN)_2$ is about 4.23 BM (Table I). This value falls between the spin-only values expected for low-spin (one unpaired electron) and high-spin (five unpired electrons) manganese(II) octahedral complexes and therefore also indicates that the substance contains bridging cyanide ligands.

Potassium Pentacyanonitrosylvanadate(−I) Monohydrate and Hydrogen.—Following removal of hydrate water at 100°, reaction with hydrogen was effected at 200°. Ammonia and a little nitrous oxide are evolved at the latter temperature and a pink solid remains after reaction is complete. The quantities of ammonia formed were not constant but were in the range corresponding to 0.2–0.5 equiv of nitric oxide in three experiments.

On the basis of analysis, the pink solid is assigned the formula $K_5V(CN)_5$. *Anal.* Calcd for $K_5V(CN)_5$: K, 51.93; V, 13.53. Found: K, 51.89 ± 0.03; V, 13.71 ± 0.04. This material is the only one of our various products which exhibits any appreciable solubility in water, about 0.2 g/100 ml. A small amount of free cyanide ion can be detected in the aqueous solution, indicating that some hydrolysis occurs. However the compound can be recrystallized unchanged by the addition of a large amount of ethanol to the aqueous solution. Acidification of the aqueous solution instantly yields a yellow solution, and moderately concentrated sulfuric acid effects immediate oxidation to

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the blue vanadyl ion. The solid compound does not appear to be at all air sensitive.

Surprisingly, $K_5V(CN)_5$ is diamagnetic; no evidence for paramagnetism is observed, even after diamagnetic corrections are made for potassium and cyanide. Since it would be expected that a complex of vanadium(0) would have either one or five unpaired electrons, the diamagnetism argues against the presence of the $[V(CN)_5]^{5-}$ ion in the solid compound and indicates that a species of higher order is formed in which there is strong vanadium–vanadium interaction. The diamagnetism calls to mind a similar situation for the nickel(I) complex of empirical formula $K_2Ni(CN)_3$, which has been shown to contain $[Ni_2(CN)_6]^{4-}$, where the nickel atoms are bridged by cyanide groups.[23]

The infrared spectrum of the pink compound exhibits three bands in the C–N stretching region, at 2030, 2078, and 2175 cm^{-1} (Table I). By comparison, the starting material shows a single C–N band at 2095 cm^{-1}. Tentatively, the band at 2175 cm^{-1} is assigned to bridged C–N stretching, and those at the two lower frequencies, to terminal C–N stretching. A similar assignment has been made for $K_4Ni_2(CN)_6$ which exhibits C–N bands at 2055, 2079, and 2128 cm^{-1}.[23]

The molar conductance of a freshly prepared 10^{-3} *M* solution of $K_5V(CN)_5$ at 25° was found to be 659 ± 33 ohm^{-1} cm^{-1} (three experiments). This value is to be compared with the corresponding molar conductances obtained for a number of other cyano complexes chosen as standards: $K_3Fe(CN)_6$, 477; $K_4Fe(CN)_6$, 581; $K_4Mo(CN)_8$, 633; $K_4W(CN)_8$, 617; and $K_5V(CN)_5NO$, 634. On the basis of these data, it would be tempting to conclude that $K_5V(CN)_5$ dissociates into six ions in aqueous solution. The conductance value is, however, also consistent with ionization of a dimeric species. Many doubtlessly would find the latter possibility not very palatable since it necessitates the proposal of an ion of extremely large negative charge, $[V_2(CN)_{10}]^{10-}$. In view of the magnetic and spectral properties of the solid and recovery of the compound changed from aqueous solution, the authors regard the dimeric formulation as a distinct possibility.

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Thiocyanato Complexes of Rhodium(I)

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The synthesis of and infrared spectral studies on rhodium(I) thiocyanato compounds of the types $RhL_2(CO)(NCS)$, $RhL_3(NCS)$, $Rh_2L_4(CNS)_2$, and $(R_4N)[Rh(CO)_2(NCS)_2]$, where L is a phosphine, an arsine, a stibine, or a phosphite, are reported. In all of these complexes terminal thiocyanate is bonded through the nitrogen atom, both in the solid state and in solution. The arylarsine and phosphite thiocyanato derivatives dissociate in part in solution with the resultant formation of dinuclear, SCN-bridged complexes of the type $Rh_2(AsR_3)_2(CO)_2(CNS)_2$ and $Rh_2[P(OR)_3]_4(CNS)_2$, respectively. The latter was isolated with triphenyl phosphite.

Introduction

It has been shown that the mode of bonding of the thiocyanate ion in palladium(II) square-planar complexes depends on the nature of other ligands present therein.[1-4] However, in six-coordinate carbonyl compounds investigated in these laboratories the important factors determining the thiocyanate bond type appear to be the oxidation state of the metal[5,6] and the extent of replacement of carbon monoxide by ligands of lesser π-acceptor properties.[7] The nature of the ligand(s) present in conjunction with CO was found to influence the mode of metal–thiocyanate bonding only in those cases where steric interactions are considered important.

In order to compare more directly the results of the aforementioned studies, we have examined the bonding in a number of square-planar rhodium(I) thiocyanatocarbonyl and -noncarbonyl complexes. Reported here are the results of our investigation.

Experimental Section

Materials.—Triphenylphosphine and triphenylstibine, purchased from Metal and Thermit Co., were recrystallized from 95% ethanol. Triphenylarsine and 4-methylpyridine from Eastman Organic Chemicals, triphenyl phosphite from Matheson Coleman and Bell, and tricyclohexylphosphine from Orgmet, Inc., were used without further purification. Reagent grade potassium thiocyanate was dried at 125°.

Dimethylphenylphosphine was prepared as described by Meisenheimer, *et al.*[8] The same general procedure was used to

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