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Reactions of Potassium Tetracyanonickelate(II) with Molten Sulfur and with Potassium Tetrasulfide in Molten Sulfur

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Potassium tetracyanonickelate(II) reacts with molten sulfur at 200° C to give, after work-up of the reaction mixture and treatment with tetramethylammonium chloride, tetramethylammonium hexathiocyanato-N-nickelate(II) as the major product. At 140° C, the nickel(II) cyano complex does not react with molten sulfur but is converted to a paramagnetic, light green, apparently polynuclear material by potassium tetrasulfide in the molten solvent. The green substance has been shown to contain coordinated sulfide and some of the nickel in a higher oxidation state than the common +2. The magnetic susceptibility of the substance is reasonably interpreted in terms of the presence of paramagnetic (tetrahedral) nickel(II) and diamagnetic nickel(IV).

Introduction

In a recent paper[1] we described the behavior of potassium hexacyanoferrate(III) toward molten sulfur at 200° C. Strong evidence was presented that sulfur added to the nitrogen end of some of the ligated cyanide groups to give a dark green polymeric material containing thiofulminate (–CNS) ligand. Treatment of this material with water permitted the isolation of a pale yellow substance which on the basis of elemental analysis, infrared, magnetic susceptibility and conductance data, and thermal stability experiments was formulated as the mixed cyanide–thiofulminate complex $K_3Fe(CN)_4(CNS)_2$.

We now report the results of a study with a relatively labile transition metal cyano complex, potassium tetracyanonickelate(II). In addition to its reaction with molten sulfur, we have examined its behavior toward potassium tetrasulfide, K_2S_4, in molten sulfur under conditions where the latter is without reaction on the nickel complex. Like molecular sulfur itself, the tetrasulfide is a potential sulfur atom donor. However, it should be a much more potent oxidant and offers the possibility of oxidation of nickel to either the III or IV state. No cyano complexes containing nickel in an oxidation state greater than II have been reported.

Experimental

Materials

Nitrogen was purified by first passing it over hot copper turnings (*ca.* 350° C) and then through drying towers containing Linde 4 A molecular sieves. Sublimed sulfur (stated purity, 99.9%) was used without further treatment. All solvents were of the highest purity commercially available. Potassium tetracyanonickelate(II) was prepared from nickel(II) cyanide 4-hydrate and potassium cyanide by the method of Fernelius and Burbage.[2] Two recrystallizations from water gave practically pure potassium tetracyanonickelate(II) 1-hydrate. The hydrate was washed with ether, powdered, and dehydrated *in vacuo* at 110° C. *Anal.* Calcd for $K_2[Ni(CN)_4]$: Ni, 24.36. Found: Ni, 24.13 ± 0.04. Potassium tetrasulfide was obtained by allowing stoichiometric amounts of sulfur and potassium to react in liquid ammonia using essentially the technique described by Brauer[3] for the preparation of Na_2S. The yellow-orange solid was obtained in practically quantitative yield. *Anal.* Calcd for K_2S_4: S, 62.1. Found: S, 61.82 ± 0.17.

Analytical Procedures

Potassium was determined gravimetrically by precipitation as the tetraphenylborate salt according to the procedure of Sporck and Williams.[4] Prior to analysis, compounds that were insoluble in water were decomposed by heating with calcium hypochlorite in water and then the solution was just acidified with concentrated hydrochloric acid and boiled to remove chlorine. Sulfur content was found by oxidation to sulfate by means of bromine in alkaline solution, acidification of the resulting solution with hydrochloric acid, and precipitation of barium sulfate with barium chloride. Microanalyses for carbon and nitrogen were performed by Ms. Kathy Widiger and also by Chemalytics, Inc. Nickel was determined titrimetrically with EDTA by the method of Flaschka.[5] Prior to analysis for the metal, samples were decomposed by heating to dryness with concentrated nitric acid.

Spectral and Magnetic Measurements

Infrared spectra of products were taken in KBr pellets on a Perkin–Elmer infrared spectrometer, Model 421. The fact that essentially identical spectra were obtained for the various compounds in Nujol mulls indicated that no reaction with potassium bromide occured. Visible solution spectra were obtained on a Cary 14 recording spectrometer and diffuse reflectance spectra on solids on a Beckman DK-2A recording spectrophotometer. Magnetic susceptibility measurements were carried out at room temperature, *ca.* 25° C, by the Faraday method using the susceptibility of $Hg[Co(SCN)_4]$ as a standard. Diamagnetic corrections were made with the use of constants given by Selwood.[6]

The $K_2[Ni(CN)_4]$–S System at 200° C

The reaction between complex and sulfur (as well as that for the $K_2[Ni(CN)_4]$–K_2S_4–S system) was carried out in the apparatus described for the reaction between potassium hexacyanoferrate(III) and molten sulfur.[1] In a typical experiment 4.5 g (0.0187 mol) of finely ground $K_2[Ni(CN)_4]$ was added to the reaction flask containing 50.0 g (1.56 gatoms) of sulfur and the reactants were mixed thoroughly. The flask and its contents were immersed in an oil bath which had been heated to 200° C. During the 24-hr reaction period at approximately 200° C the system was flushed continuously with dry oxygen-free nitrogen. Qualitative tests for cyanogen in the exiting gas stream were negative. After 24 hr, the reaction mixture was allowed to cool to about 150° C and was then filtered. The gray-black solid that remained on the filter was first extracted with carbon disulfide until all residual sulfur had been removed and then with 100 ml of dry spectrograde acetone in a Soxhlet extractor. The treatment with acetone yielded an intense blue extract. Extraction was continued until the acetone extract was colorless.

The acetone extract (60–70 ml) was added to a hot solution of 75 ml of acetone and 5 ml of water containing 7.95 g (0.074 mol) of tetramethylammonium chloride. A pale blue solid separated. The mixture was boiled for 10 min and then allowed to cool to room temperature. The pale blue solid was filtered off, washed with ethanol, and dried at 50° C *in vacuo* for 12 hr; yield, 6.4 g. Part (2.0 g) of the product was dissolved in 90 ml of boiling nitromethane (*hood*). The resulting dark blue solution was filtered hot and the filtrate allowed to cool to room temperature. The pale blue crystals which formed were recovered by filtration, washed with ethanol, and dried at 50° C *in vacuo* for 12 hr; yield, 0.4 g.

The dark residue remaining in the thimble of the Soxhlet extractor was suspended in water and stirred. The undissolved solid was filtered off, giving a yellow filtrate that was shown to contain nickel and thiocyanate ions. The filtrate was concentrated and gave a yellow solid which, on the basis of infrared spectroscopy, proved to be a mixture of potassium thiocyanate and unreacted $K_2[Ni(CN)_4]$. A small amount of olive-brown solid which had adhered to the walls of the extractor thimble was identified as nickel(II) thiocyanate.

The $K_2[Ni(CN)_4]$–K_2S_4–S System at 140° C[7]

A series of runs in which the amounts of nickel complex (0.01 mol) and sulfur (1.56 gatoms) were held constant and the amount of K_2S_4 was varied from 2 X 10^{-5} to 0.02 mol, showed that the mole ratio of $K_2S_4:K_2[Ni(CN)_4]$ had very little effect on the amount of nickel-containing product obtained. The maximum yield of the latter isolated, 0.7 g, was obtained in an experiment in which the mole ratio of $K_2S_4:K_2[Ni(CN)_4]$ was 10:2.5. In an experiment where this ratio was 1:500, the yield of nickel-containing product was 0.4 g.

In each reaction, the complex, potassium tetrasulfide, and sulfur were mixed in an argon atmosphere since the polysulfides are air- and moisture-sensitive. The reaction flask was placed in an oil bath which had been heated to 140° C, and the mixture was maintained at this temperature, with stirring, for 24 hr. Dry, oxygen-free nitrogen was passed over the reactants continuously and the exiting gas was tested for cyanogen with negative results.

Following the 24-hr reaction period, the mixture was filtered (the sulfur filtrate gave no test for cyanide ion). The crude solid product on the filter was extracted with 95% ethanol in a Soxhlet extractor for about 12 hr. Usually after the period of extraction, bright green crystals appeared in the extractor pot. These were filtered off and the ethanol filtrate was returned to the extractor pot. After about 12 additional hours of extraction, additional green crystals were isolated from the pot. The procedure was repeated for 12-hr periods so long as crystals were obtained. The total time of extraction was usually between 48 and 72 hr. The solid material remaining in the extraction thimble was shown to be a mixture of unreacted $K_2[Ni(CN)_4]$ and an unidentified sulfur-containing material which gave no infrared absorptions in the 4000–550 cm^{-1} region.

The green crystals were stirred with 50-ml portions of carbon disulfide until elementary sulfur was no longer extracted. They were then stirred with 50-ml portions of water at room temperature until removal of starting complex was complete. The green product was finally dried *in vacuo* at 120° C for 12 hr. On standing in air, even for long periods of time, its appearance and infrered spectrum did not change.

Results and Discussion

The $K_2[Ni(CN)_4]$–S System

The major product isolated from the reaction of $K_2[Ni(CN)_4]$ with sulfur after the work-up described and treatment with tetramethylammonium chloride was identified as tetramethylammonium hexathiocyanato-N-nickelate(II). *Anal.* Calcd. for $[(CH_3)_4N]_4[Ni(NCS)_6]$: Ni, 8.34; C, 37.55; N, 19.90; H, 6.87. Found: Ni, 8.21 ± 0.03; C, 37.70 ± 0.05; N, 19.69 ± 0.00; H, 7.05 ± 0.09. Magnetic measurements on two different samples of the pale blue compound gave effective magnetic moments of 3.39 B.M. (297° K) and 3.17 B.M. (293.5° K). The effective magnetic moment for a closely related compound $[(C_2H_5)_4N]_4[Ni(NCS)_6]$ is 3.25 B.M., which is in the range commonly found for the magnetic moments of octahedral nickel(II) complexes.[8] The infrared spectrum of the recrystallized product exhibited the following absorptions: 3020(m), 2957(m), 2874(m), 2094(vs), 1480(vs), 1412(s), 1280(w), 941(vs), and 774 (s) cm^{-1}. Forster and Goodgame[8] reported bands at 2096(vs) and 777 (w) cm^{-1} for $[(CH_3)_4N]_4[Ni(NCS)_6]$, which they attributed to the C–N and C–S stretching modes, respectively, of N-bonded thiocyanate.

It is interesting that tetramethylammonium hexathiocyanato-N-nickelate(II) was isolated from an acetone solution which had a visible absorption spectrum virtually identical to that reported for $[Ni(NCS)_4]^{2-}$ in the same solvent.[8] Moreover, when the hexathiocyanato complex was redissolved in acetone, the spectrum obtained was that of the tetrathiocyanato species.

Our results, of course, leave open the matter of what actually occurs in the reaction mixture. Does sulfur add initially to the nitrogen atom of bound cyanide, as it does with hexacyanoferrate(III), and does the product undergo rearrangement? Is the tetracyano complex sufficiently labile in molten sulfur that addition of the latter to cyanide ion and not to the complex occurs? Is the original complex product four- or six-coordinate or does the six-coordinate material result from the manner of work-up of the reaction mixture?

The $K_2[Ni(CN)_4]$–K_2S_4–S System

The bright green product isolated from this system in each case was insoluble in water and all common organic solvents at room temperature, even on prolonged stirring. Elemental analysis showed the presence of hydrogen, which on the basis of the following infrared information was attributed to lattice water. The material gave bands at 3610(s), 3400(w, br), 1610(m), and 1595(m) cm^{-1}. These bands remained even after prolonged heating *in vacuo* at 120° C. The absence of bands in the 880–650 cm^{-1} region, normally attributed to the rocking mode of coordinated water,[9] indicates that the water is not bound to nickel.

Elemental analyses on the green products from five different experiments gave the following results: (1) K, 15.32 ± 0.11; Ni, 33.28 ± 0.17; S, 4.78 ± 0.03; C, 18.43 ± 0.16, N, 22.16 ± 0.21; H_2O (from percentage of hydrogen), 6.77. (2) K, 16.43 ± 0.20; Ni. 31.73 ± 0.18; S, 5.69 ± 0.08; C, 18.64 ± 0.10, N, 20.77 ± 0.13; H_2O, 8.03. (3) K, 13.98 ± 0.21; Ni, 34.13 ± 0.11; S, 6.00 ± 0.21; C, 18.79 ± 0.14; N, 20.82 ± 0.16; H_2O, 6.23. (4) K, 15.19 ± 0.10; Ni, 31.20 ± 0.05; S, 5.57 ± 0.02; C, 19.45 ± 0.22; N, 20.88 ± 0.10; H_2O, 7.20. (5)[10] K, 16.33 ± 0.25; Ni, 32.78 ± 0.25; S, 4.27 ± 0.13; C, 18.73 ± 0.21; N, 22.00 ± 0.24; H_2O, 4.17. The following empirical formulas were calculated from these data: (1) $K_{2.6}Ni_{3.8}S_{1.0}(CN)_{10.5} \cdot 2.5H_2O$; (2) $K_{2.4}Ni_{3.1}S_{1.0}(CN)_{8.6} \cdot 2.5H_2O$; (3) $K_{1.9}Ni_{3.1}S_{1.0}(CN)_{8.2} \cdot 1.9H_2O$; (4) $K_{2.2}Ni_{3.1}S_{1.0}(CN)_{8.9} \cdot 2.3H_2O$; and (5) $K_{3.1}Ni_{4.2}S_{1.0}(CN)_{11.8} \cdot 1.7H_2O$.

In contrast to the diamagnetic character of the potassium tetracyanonickelate(II) starting compound, the green products were paramagnetic, with gram magnetic susceptibilities ($\chi_g \times 10^6$ cgs units) of (1) 8.1661; (2) 7.4508; (3) 6.8027; (4) 6.7597; and (5) 5.5756 for the five products for which the analytical data are shown. These values yielded effective magnetic moments ranging from 3.03 to 3.70 Bohr magnetons, based on the empirical formulas noted (Table I).

The infrared spectrum of the product was identical from run to run. In addition to the absorptions attributed to lattice water, the following bands were found: 2148(s); 2092(vs); 2058(vs); 2037(sh); 436(s); and 285 (w) cm^{-1}.

The insolubility of the green products and the variable empirical formulas (coupled with the identity of the infrared spectra) strongly suggest that the products

TABLE I. Experimental Effective Magnetic Moments *vs.* Calculated Moments for Tetrahedral Ni(II)[a]–Ni(IV) Mixtures.

Empirical Formula	Ave. Oxid. No. of Nickel	Mole Fraction		Effective Magnetic Moment, B.M.	
		Ni(II)	Ni(IV)	μ_{cald}	μ_{exptl}
$K_{2.6}Ni_{3.8}S_{1.0}(CN)_{10.5} \cdot 2.5H_2O$	2.61	69.5	30.5	2.92–3.50	3.70
$K_{2.4}Ni_{3.1}S_{1.0}(CN)_{8.6} \cdot 2.5H_2O$	2.65	67.5	32.5	2.88–3.45	3.19
$K_{1.9}Ni_{3.1}S_{1.0}(CN)_{8.2} \cdot 1.9H_2O$	2.68	66.0	34.0	2.84–3.41	3.03
$K_{2.2}Ni_{3.1}S_{1.0}(CN)_{8.9} \cdot 2.3H_2O$	2.80	59.5	40.5	2.70–3.24	3.12
$K_{3.1}Ni_{4.2}S_{1.0}(CN)_{11.8} \cdot 1.7H_2O$	2.55	72.5	27.5	2.98–3.58	3.20

[a] The effective magnetic moment for tetrahedral Ni(II) was assumed to be 3.5–4.2 B.M.

are polynuclear. Additional support for polynuclear character is found in the results of calculations of the "average" coordination number of the nickel. On the assumption that the sulfur in the products is present as coordinated sulfide (an assumption that is justified below), the average coordination number of nickel ($S^{2-}+CN^{-}/Ni$) for the five products is 3.07 ± 0.06. Transition metal complexes in which the central metal atom apparently has a coordination number of three are usually polynuclear, *e.g.*, $AuCl_3$, $CsCuCl_3$; the sharing of ligands gives the metal a coordination number greater than three.

The evidence that sulfur is bonded as sulfide is strong. The infrared bands at 2148, 2092, 2058 and 2037 cm^{-1} are assigned to C–N stretching modes and the band at 436 cm^{-1} to a Ni–C≡N bending mode. Were sulfur present as Ni–CNS, an N–S stretching band would have been observed in the 680–1500 cm^{-1} region,[11] but no such band occurs. If sulfur were present as either S- or N- bonded thiocyanate ligand, a C–S stretching band would have been found in the 680–860 cm^{-1} region.[12] The presence of sulfur as polysulfide is excluded because the S:Ni ratio, as shown by the elemental analysis, is much too low. The appearance of the weak absorption peak at 285 cm^{-1} is evidence that the sulfur is present as sulfide ligand. Metal–sulfur stretching frequencies generally occur in the 400–230 cm^{-1} region[13] and are usually of weak or medium intensity.

In addition to the spectral evidence, support for the presence of sulfide in the green material comes from its behavior toward boiling water. When suspended in this medium for about five minutes, the substance was converted to a light blue solid which was identified as nickel(II) cyanide. The solution gave positive tests for *sulfide* and *cyanide* ions, but not for thiocyanate.

Charge balance calculations, on the basis that the ligands bound to nickel are cyanide and sulfide, give average oxidation numbers for the metal ranging from 2.55 to 2.81 for the five samples the empirical formulas of which are given above. It would thus appear that some of the dipositive nickel in the original complex has been oxidized and the question arises whether the higher oxidation state is best representated as III or IV.

Electronic spectral data are of little help in characterizing the higher oxidation state of the nickel. The reflectance spectrum of the green product was identical for each preparation and showed a very strong band at 25.8 kK and a weaker one at 17.4 kK. We can offer no interpretation for these bands. Very little information on the visible and ultraviolet spectra of nickel(III) and nickel(IV) complexes has been reported. Moreover, the polynuclear character of the green product and the presence of substantial nickel(II) make for an extremely complicated situation.

The determination of the nature of the higher oxidation state of the nickel was approached through an analysis of the calculated average oxidation number of the metal and observed magnetic moments of the products isolated. If the intra- and intermolecular magnetic interactions are sufficiently small so that a polynuclear complex behaves magnetically as though it were a mixture of mononuclear species, the complex should have a magnetic moment (per metal atom) which is equal to the root-mean-square of the magnetic moments of the species present.[14]

It was assumed that the green product was a mixture of either nickel(II) and nickel(III) or nickel(II) and nickel(IV) species. For each of the five products for which complete analytical data were used to assign empirical formulas, the mole fractions of nickel(II) and nickel(III) or nickel(IV) were calculated from the average oxidation number. Then the theoretical effective magnetic moments of combinations of tetrahedral, square planar, and octahedral nickel(II) with nickel(III) and with nickel(IV) were calculated with the use of the root-mean-square relationship and compared with experimentally determined values based on the empirical formulas of the green products. Regular tetrahedral nickel(II) complexes exhibit effective magnetic moments in the range 3.5–4.2 Bohr magnetons; the square planar complexes are diamagnetic, and the octahedral complexes have moments in the range 2.9–3.4 Bohr magnetons.[15] Nickel(III) has one unpaired electron in square planar, trigonal bipyramidal, tetragonal, or octahedral (strong field) complexes, and consequently the values 1.7–1.9 Bohr magnetons were used for these possibilities. For nickel(III) in a tetrahedral environment, an as yet unreported three-unpaired electron species, the value 3.87 Bohr magnetons was used for the effective moment. Nickel(IV) complexes are either diamagnetic or weakly paramagnetic. In the calculations, nickel(IV) was assumed to be diamagnetic.

Of all the Ni(II)–Ni(III) and Ni(II)–Ni(IV) combinations, only one, tetrahedral nickel(II) and diamagnetic nickel(IV), gave generally good agreement between experimental and calculated magnetic moments. The comparative data for the tetrahedral nickel (II)–diamagnetic nickel(IV) combination are shown in Table I and clearly make a strong case for the hypothesis that these species are present in the green product.

Moreover, it is reasonable to expect that elemental sulfur in oxidation of dipositive nickel would function as a two-electron rather than a one-electron oxidant. Finally, if our interpretation of the nature of the green product is correct, it indicates that replacement of a small fraction of the strong field cyanide ligands by the much weaker field sulfide is accompanied by pronounced alteration in the geometrical environment of the nickel(II).

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