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Proton Relaxation Times and Spectrophotometric Characteristics of Solutions Containing Pentacyanonickelate Ions

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Received August 19, 1963

The proton relaxation times of aqueous solutions of tetracyanonickelate containing varying amounts of cyanide have been measured by several methods using high-resolution n.m.r. spectrometers. The relaxation time was found to be equal to that of the solvent with no indication of the formation of paramagnetic higher complexes. Spectrophotometric studies of tetracyanonickelate solutions in the presence of excess cyanide showed the presence of the pentacyanonickelate ion with a stepwise formation constant of 0.21 l./mole at 23° at an ionic strength of 2.5 *M*.

Blackie and Gold[1-3] measured the spin-lattice relaxation time, T_1, of the protons in an ammoniacal aqueous solution of nickel cyanide containing various amounts of cyanide by means of a broad band (low resolution) n.m.r. spectrometer. The relaxation times were measured either by the direct or by the progressive saturation method, the latter being used in the same way as by Bloembergen, Purcell, and Pound.[4] From their results they concluded that the hexacyanonickelate ion is formed quantitatively by the addition of two equivalents of cyanide to a solution of the tetracyanonickelate containing ammonia, and that the hexacyanonickelate ion, although not paramagnetic, acted as a catalyst for the spin-lattice relaxation process with an effective magnetic moment of 1.58 B.M. These results are surprising for at least two reasons. First, their n.m.r. titration curve of nickel with cyanide implies a quantitative formation of hexacyanonickelate with a stepwise formation constant from the tetracyanonickelate of the order of 10^{10}, although analytical chemists have for many years titrated nickel with cyanide to the tetracyanonickelate with no evidence of higher complex formation.[5] Neither is it likely that addition of two weakly held cyanide groups would produce the change to octahedral symmetry needed for a paramagnetic species [there is ample evidence for the existence of diamagnetic penta- and hexacoordinated Ni(II)],[6] nor that such a drastic catalysis of the spin-lattice relaxation process could be afforded by a diamagnetic species. In view of this, the present investigation was undertaken to repeat and extend their work.

Experimental

Materials.—Reagent grade chemicals were used directly when available. Nickel cyanide was prepared from nickel sulfate and sodium cyanide. The product was found to contain 1.53 moles of water per nickel atom after prolonged drying at room temperature and gave negative tests for sulfate and free nickel ions. The dried product was analyzed by dissolving it in a slight excess of standardized sodium cyanide solution, back-titrating the excess cyanide with silver nitrate, according to the standard Liebig–Denigès method.[5,7] It was found that 110.7 g. (1 mole) of the anhydrous product reacted with 2.01 moles of cyanide. Sodium tetracyanonickelate, $Na_2Ni(CN)_4 \cdot 3H_2O$, was prepared from the nickel cyanide by using slightly less than the equivalent amount of sodium cyanide.[8] The yellow needles were free of sulfate and of theoretical composition. Stock solutions of sodium cyanide were analyzed by direct titration with silver nitrate and by the method of Liebig–Denigès. The results with the latter method were on the average about 0.3% lower, in agreement with a calculation of the titration error.[7] Nickel cyanide solutions in 5.0 *M* ammonia were found to be stable. If sodium cyanide were added, however, the excess cyanide was found to decompose slowly so that the solution had to be used within a few days. The hydrolysis of the cyanide was followed by titrating the amount remaining by the Liebig–Denigès method after evaporation of the bulk of the ammonia. At 23°, in solutions containing 33.5 m*M* Ni and 5.0 *M* NH_3, the hydrolysis followed the first-order rate law

$$-d(CN/Ni)/dt = 9 \times 10^{-3}[CN/Ni - 2] \text{ days}^{-1}$$

In solutions containing only sodium cyanide and ammonia, the decomposition is very much slower. Stock solutions of sodium perchlorate were analyzed by replacing the sodium with hydrogen ion using Dowex 50 cation exchanger in the hydrogen form and titrating with standard sodium hydroxide. The concentration calculated from the density agreed with the analytical concentration within 1.2%.

Apparatus.—For most of our measurements a Varian A60 high resolution n.m.r. spectrometer was used. Details of the techniques by which relaxation times may be measured on the instrument are being described in detail elsewhere.[9] The spin lattice relaxation time, T_1, was measured by the direct method.[10] The exponential grow-in of the n.m.r. signal, which is observed when the amplitude of the radiofrequency field is suddenly changed from a high saturating value to a low nonsaturating value, was measured with a Sanborn 151–100A recorder, driven by a Sanborn 150–1800 amplifier. To switch the radiofrequency field from a high to a low amplitude, a radiofrequency attenuator with a constant input and output impedance of 90 ohms was used (Boonton M 602) instead of the attenuator belonging to the A60. Good time traces were obtained when the sample was not spun.

Relaxation times longer than 1 sec. reproduced within 5%. The direct method is most accurate for longer relaxation times but becomes increasingly uncertain for T values below 50 msec.

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TABLE I

PROTON SPIN RELAXATION TIMES

Solution	CN/Ni	[Ni], m*M*	[NH$_3$], *M*	T_1 direct	T_1 spin-echo	$\sqrt{T_1T_2}$ prog. sat.	T_2 line-width	T_2 spin-echo
H_2O	...	...	...	2.8	2.2	1.3	...	...
NH_3	...	...	5.0	2.7	...	...	...	0.9
$NiSO_4$	...	20	...	0.091	...	0.076	0.052	...
$NiSO_4$	...	33.5	...	...	...	...	...	0.027
$NiSO_4$	...	15.7	4.9	0.075	...	...	0.017	...
$NiSO_4$	...	33.4	4.9	0.032	...	0.015	0.0068	...
$Ni(CN)_2$	2.0	33.5	5.0	0.069	...	0.033	0.013	0.016
$Ni(CN)_2$ + KCN	3.0	33.5	5.0	0.143	...	0.066	0.028	0.028
$Ni(CN)_2$ + KCN	4.0	33.5	5.0	2.1	...	...	>0.5	...
$Ni(CN)_2$ + KCN	4.5	33.5	5.0	2.7	...	...	>1	1.0
$Ni(CN)_2$ + KCN	5.0	33.5	5.0	2.8	..	...	>1	0.9
$Ni(CN)_2$ + KCN	6.0	33.5	5.0	2.8	..	...	>1	...
$Ni(CN)_2$ + KCN	8.0	33.5	5.0	2.7	...	...	>1	...
$Na_2Ni(CN)_4$	4.0	33.5	5.0	...	...	...	...	0.8
$NiSO_4$ + NaCN	6.0	100	...	...	2.2	...	...	...
$NiSO_4$ + NaCN	7.0	100	...	...	2.1	...	...	...
$NiSO_4$ + NaCN	8.0	100	...	...	2.2	...	...	...

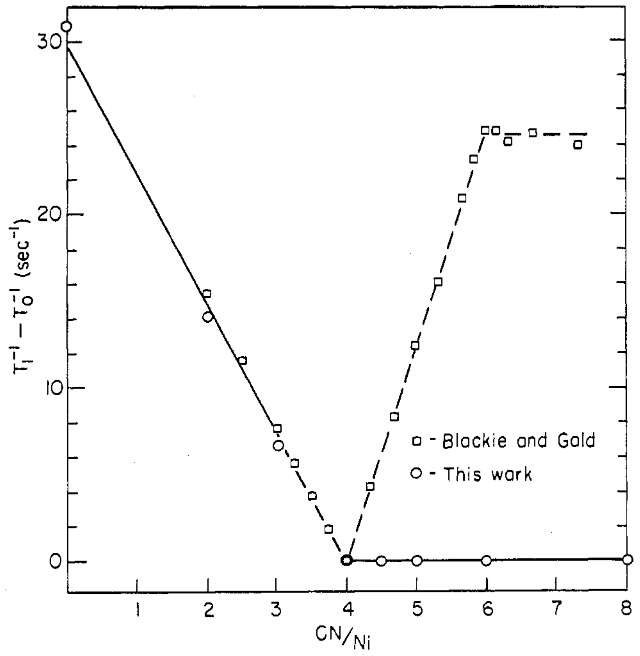

Fig. 1.—Proton relaxation in ammoniacal solutions of nickel and cyanide as found by Blackie and Gold[2] and in the present investigation.

Thus, at T_1 = 34 msec. the standard deviation was 14%. The transverse relaxation time, T_2, was obtained from the full line width, $\nu_{1/2}$, at half height: $T_2 = 1/\pi\nu_{1/2}$. Correction was made for the inhomogeneity of the magnetic field. Because of the inhomogeneity, the width of the water line was usually about 0.7 c.p.s. The line-width technique is most useful in the 5–500 msec. range and T_2 reproduces within about ±2%. Longer relaxation times can be estimated only roughly.

The progressive saturation method[10] was also used. Here $\sqrt{T_1T_2}$ is calculated from the height of the partially saturated peak, giving suitable relative values. The relaxation times, T_1 and T_2, were also measured by the spin-echo technique, utilizing here a Varian 56.4 Mc. n.m.r. spectrometer converted for Carr–Purcell spin-echo experiments[11] following the modifications suggested by Meiboom and Gill.[12]

Spin-echo measurements of T_2 were internally consistent and led to the same qualitative interpretations as T_1 measurements by the direct method although the absolute values were considerably lower. This is an effect commonly observed in spin-echo T_2 work and has not as yet been satisfactorily explained.

Exploratory spectrophotometric measurements were made using a Cary Model 11 spectrophotometer. Quantitative measurements for the determination of the formation constant were made with a Beckman DU spectrophotometer at 425 mμ, using 1-cm. quartz cells.

Results and Discussion

Relaxation time measurements were made on air-saturated solutions at a temperature of 37.8 ± 1.4°. The solutions were prepared by dissolving known amounts of nickel cyanide, $Ni(CN)_2$, in aqueous ammonia, adding a solution of potassium cyanide, and making up to exact volume with water. From the results in Table I, it is evident that the solutions for which the ratio of cyanide to nickel is greater than four have the same relaxation time as the solvent, in sharp contrast with the findings of Blackie and Gold. In the absence of ammonia, the results are entirely similar. The relaxation times of solutions for which the ratio of cyanide to nickel is smaller than four corresponds to a mixture of paramagnetic nickel ammonia complex with the diamagnetic tetracyanonickelate. Interestingly, the two relaxation times, T_1 and T_2, are not the same for the nickel–ammonia complex, being in a ratio of approximately 5 : 1. This somewhat unusual phenomenon has previously been observed for the Mn(II), Gd(III), and Co(II) ions.[13] The measurements by Blackie and Gold were obtained by titrating an aqueous solution initially 0.1 *M* in nickel cyanide and 17 *M* in ammonia with 0.1 *M* potassium cyanide until the ratio of total cyanide to total nickel was 4 : 1. From there on they continued the titration with a solution supposedly containing 0.033 *M* potassium cyanide. In the course of the experiment the original solution was diluted more than tenfold. Even allow-

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ing for the error which must certainly be introduced in using a factor of 10 as the correction factor for dilution, it is difficult to see how their results could be obtained. The contrast between the present results and previous findings is shown in Fig. 1.

It was observed in working with solutions of tetracyanonickelate in excess cyanide that increasing concentrations of cyanide ion changed the yellow color of the tetra complex to a deep orange. The absorption spectrum between 300 and 520 mμ is altered markedly by a large excess, and at 425 mμ the extinction coefficient is increased by a factor of about 50. The absorbance of 0.4 to 70 mM solutions of sodium tetracyanonickelate was measured at 425 mμ in media ranging from 0.05 to 2.5 M sodium cyanide, the ionic strength being held constant at 2.5 M by addition of sodium perchlorate as needed. The data were treated by the well-known method of McConnell and Davidson,[14] yielding an excellent straight line. Least-squares fitting of this line led to a preliminary value of 0.201 ± 0.009 l./mole for the stepwise formation constant of pentacyanonickelate. Correcting for the hydrolysis of the cyanide ion in these solutions, the value becomes 0.205 ± 0.009 l./mole at 23° and an ionic strength of 2.5 M. The extinction coefficient, ϵ_5, was found to be 334 ± 15 l./mole cm. at 425 mμ. These results confirm the infrared work of McCullough, Jones, and Penneman,[15] which appeared just as we were completing this phase of the investigation and are in harmony with their more recent infrared study of the same system[16] in which they found evidence of a very weak hexacyano complex existing at cyanide concentrations greater than 2.5 M. Beck and Bjerrum[17] from spectrophotometric evidence also concluded that the pentacyanide complex is produced when excess cyanide is added to the nickel tetracyanide solutions. A previous effort had been made by Kišova and Čuprova[18] to interpret the absorption of light by mixtures of the complex cyanides of copper(I) and nickel(II) in terms of a nickel hexacyanide complex. Their results were ambiguous, however, and re-examination of their continuous variations data shows clear evidence of a pentacyanonickelate rather than a hexacyanonickelate being formed.

An attempt was made by Blackie and Gold[19] to determine the stability constant of the hexacyanonickelate ion by measuring the equilibrium constants of several reactions supposedly involving this species. Proton relaxation times were determined and the equilibrium concentrations of Ni(CN)$_6^{-4}$ calculated on the assumption that it was the only species contributing to the relaxation. The results were quite contradictory, and in view of the findings in the present investigation, it does not now seem likely that the discrepancies were due to inconsistences in Latimer's tables[20] as had been suggested.

Acknowledgment.—We gratefully acknowledge the many helpful discussions with Dr. Rolf W. Arndt, who also did the spin-echo and some of the line width measurements. This work was supported in part by the United States Atomic Energy Commission under Contract AT(30-1)-905.

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