809. *A Magnetic Investigation of Cyanide Complexes of Nickel*(II) *in Solution.*

By M. S. Blackie and V. Gold.

Measurements of spin–lattice relaxation times of solvent protons by means of a wide-band nuclear magnetic resonance spectrometer have been used in a study of some cyanide complexes of nickel(II). The solution of nickel(II) cyanide in aqueous ammonia contains nickel entirely in the form of equimolecular amounts of $Ni(NH_3)_6^{2+}$ and $Ni(CN)_4^{2-}$ ions. Addition of potassium cyanide to this solution brings about a quantitative conversion of $Ni(NH_3)_6^{2+}$ into $Ni(CN)_4^{2-}$, the tetracyano-complex being the only nickel-containing species in solution when the stoicheiometric ratio CN/Ni is 4. Addition of cyanide beyond this point results in quantitative formation of $Ni(CN_6)^{4-}$, which is a catalyst for the relaxation of solvent protons about as effective as $Ni(NH_3)_6^{2+}$. When the stoicheiometric ratio CN/Ni is 6, all the nickel is in the form $Ni(CN)_6^{4-}$ and further cyanide addition up to a CN/Ni ratio of 7·33 is without effect.

Since magnetic-susceptibility measurements of aqueous solutions corresponding to the solute composition $K_4Ni(CN)_6$ have shown the presence of little, if any, paramagnetic solute, the observations indicate the occurrence of efficient spin–lattice relaxation involving a non-paramagnetic species.

The interconversion of diamagnetic and paramagnetic species in solution can be detected by the change in the apparent magnetic moment of the solute. This can be measured either by determining the bulk susceptibility of the ionic solution or by observing the spin–lattice relaxation time of the solvent protons by proton magnetic resonance spectroscopy.[1]

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[1] Bloembergen, Purcell, and Pound, *Phys. Rev.*, 1948, **73**, 679.

The second technique is particularly suitable for the investigation of dilute solutions, since the phenomenon observed is a direct measure of the concentration and effective moment of the solute and not, as in bulk susceptibility measurements, a sum of solvent and solute susceptibilities. In the present work, nuclear magnetic resonance measurements of this kind have been applied to problems in the co-ordination chemistry of nickel(II), *viz.*, (i) the nature of the solution formed by dissolving nickel(II) cyanide in aqueous ammonia, and (ii) the species formed on addition of potassium cyanide to this solution and the equilibrium between them.

Experimental.—The construction and calibration of the nuclear magnetic resonance spectrometer and its adaptation for the measurement of proton relaxation times of aqueous solutions have been described.[2] The relaxation times were measured by either the " direct " or the " progressive saturation " method. Measurements by the former technique were restricted to relaxation times somewhat greater than 1 sec. The relaxation time was accurately related to the concentration of a relaxing species by the accepted equation [1] (see also ref. 2).

$$T_1^{-1} - T_0^{-1} = \alpha\mu_N^2 c \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where T_1 and T_0 are the relaxation times for the solution and the solvent respectively, and c is the concentration of the relaxing solute. For most measurements $T_1^{-1} \gg T_0^{-1}$. According to theory [1,3] μ_N is the effective magnetic moment of the paramagnetic relaxing solute, and α is a constant the value of which for water was obtained for our purposes by calibration of the apparatus with cupric ions for which μ_N was taken to have the value [4] 2·00 B.M. For the ammoniacal solutions the cuprammonium ion (as sulphate) with a reported [5] μ_N of 1·51 B.M. was used for all calibration. The values of α for the two media agree within experimental error.

TABLE 1. *Proton relaxation times for solutions of* $Ni(CN)_2,4H_2O$ *in aqueous ammonia* (*d* 0·880).

[Ni(II)] (M)	0	0·001	0·005	0·010	0·050	0·100
T_1 (obs.) (msec.)	5700	1600	400	215	44	21·5
$T_1^{-1} - T_0^{-1}$ (sec.$^{-1}$)	—	0·45	2·32	4·47	22·6	46·3

TABLE 2.

KCN added (mmoles)	CN/Ni	Vol. (V) of soln. (ml.)	$[Ni(NH_3)_6^{2+}]$ (calc.) (M)	$[Ni(CN)_6^{4-}]$ (calc.) (M)	10^3T_1 (sec.)	$T_1^{-1} - T_0^{-1}$ (sec.$^{-1}$)	$(T_1^{-1} - T_0^{-1})V/V_0$ (sec.$^{-1}$)
0	2·00	1·00	0·0500	—	21·5	46·3	46·3
0·050	2·50	1·50	0·0250	—	43	23·1	34·6
0·100	3·00	2·00	0·0125	—	85	11·6	23·2
0·125	3·25	2·25	0·0085	—	130	7·5	16·9
0·150	3·50	2·50	0·0053	—	215	4·5	11·2
0·175	3·75	2·75	0·0022	—	450	2·0	5·6
0·200	4·00	3·00	—	—	4800	0·03	0·1
0·233	4·33	4·00	—	0·0040	290	3·3	13·0
0·267	4·67	5·00	—	0·0066	195	5·0	24·8
0·300	5·00	6·00	—	0·0083	155	6·3	37·6
0·333	5·33	7·00	—	0·0095	140	7·0	48·3
0·367	5·67	8·00	—	0·0104	125	7·8	62·6
0·384	5·84	8·50	—	0·0108	120	8·2	69·3
0·400	6·00	9·00	—	0·0111	115	8·5	74·4
0·417	6·17	9·50	—	0·0105	125	7·8	74·4
0·433	6·33	10·00	—	0·0100	135	7·2	72·3
0·467	6·67	11·00	—	0·0091	145	6·7	73·9
0·533	7·33	13·00	—	0·0077	175	5·5	71·9

All measurements of proton relaxation times were performed with sample volumes of 0·23 cm.³ at room temperature (18—20°). Chemicals used were of " AnalaR " grade or otherwise of high purity. In all cases the level of paramagnetic impurities was insignificant.

The effect of added cyanide upon ammoniacal solutions of nickel(II) cyanide was studied

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[2] Blackie, *Trans. Faraday Soc.*, in the press.

[3] Solomon, *Phys. Rev.*, 1955, **99**, 559.

[4] Conger and Selwood, *J. Chem. Phys.*, 1952, **20**, 383.

[5] Rivkind, *Doklady Akad. Nauk S.S.S.R.*, 1954, **98**, 97.

by making additions of different amounts of potassium cyanide solution from a micrometer syringe to 1 ml. portions of 0·1M-nickel solution. Table 2 indicates both the volumes used and the stoicheiometric concentrations achieved. Measurements on solutions were taken approximately ½ hr. after each addition of cyanide to ensure mixing and equilibration. Relaxation times were in fact constant and reproducible from about 15 min. after addition of cyanide. The results are given in Table 2.

DISCUSSION

Table 2 shows that the relaxation time increases as cyanide ions are added to the ammoniacal solution of nickel(II) cyanide, up to the point where the concentration of cyanide groups in solution is four times that of nickel. On further addition of potassium cyanide the relaxation time decreases. This means that the first part of the cyanide addition removes relaxing ions until, when the ratio CN/Ni is 4, and the proton relaxation time is practically the same as for aqueous ammonia, the solution contains only diamagnetic species in significant amounts. The diamagnetism of all solutes at this stage is to be expected, since $Ni(CN)_4^{2-}$ is a diamagnetic ion and the reported value of its stability constant [6,7] requires that less than 0·1% of the nickel would be present in the form of the "free" (or aquated) nickel(II) ion. Our measurements thus confirm the low concentration of these ions (cf. ref. 8).

Since nickel(II) cyanide $[NiNi(CN)_4]$ is insoluble in water but soluble in aqueous ammonia, it seemed probable that an ammoniacal solution of nickel cyanide would contain nickel in the form of the ions $Ni(NH_3)_6^{2+}$ and $Ni(CN)_4^{2-}$. The hexammine is paramagnetic and is therefore expected to be the relaxing species which disappears during the first stage of the cyanide addition. This conclusion is supported by a comparison of the relaxation times of ammoniacal solutions of nickel(II) cyanide and of hexamminenickel(II) sulphate. The relaxation time in a nickel(II) cyanide solution is found to be the same as that in a hexamminenickel(II) sulphate solution [2] of half the total nickel concentration (Fig. 1). This means that in the ammoniacal solution ammonia molecules do not displace any of the cyanide ligands of the tetracyanonickelate(II) ion.

By making the assumption that the reaction

$$Ni(NH_3)_6^{2+} + 4CN^- \longrightarrow Ni(CN)_4^{2-} + 6NH_3$$

is stoicheiometrically complete at all stages of cyanide addition (and that no other complexes have to be considered during the destruction of the hexammine) it is possible to calculate the concentration of the paramagnetic hexamminenickel(II) ion at every stage. This very simple hypothesis is quantitatively confirmed by comparing the relaxation times of the solutions at the calculated concentrations with the measurements [2] on ammoniacal solutions of hexamminenickel(II) sulphate (Fig. 1).

The decrease in relaxation time which is found on addition of cyanide ions beyond the tetracyano-stage indicates the formation of another species capable of catalysing the proton-relaxation process. For the quantitative interpretation of these measurements it is necessary to allow for the fact that the addition of potassium cyanide solution not only raises the CN/Ni ratio in the solution but also causes a diminution of the overall nickel concentration by dilution. Since $(T_1^{-1} - T_0^{-1})$ is proportional to the concentration of relaxing ions [eqn. (1)], the dilution effect can be allowed for by multiplying all values of $(T_1^{-1} - T_0^{-1})$ by V/V_0 where V is the total volume of solution after cyanide addition and V_0 the initial volume of the nickel solution. In this way all measurements are related to the concentration of the initial solution of $[Ni(NH_3)_6]^{2+}[Ni(CN)_4]^{2-}$. The corrected values of $(T_1^{-1} - T_0^{-1})$ are given in the last column of Table 2 and related to the CN/Ni ratio in Fig. 2. The first, downward portion of the curve again illustrates the conversion of

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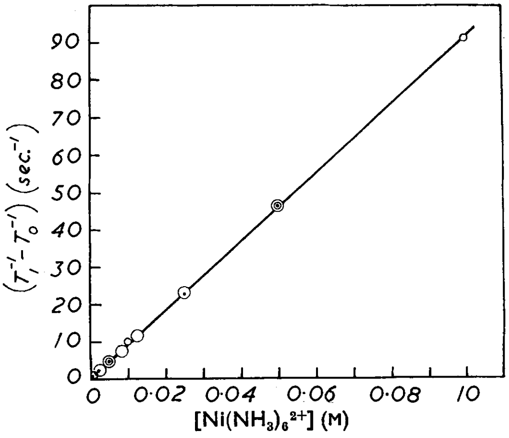
[6] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd edn., Prentice-Hall, New York, 1952, p. 200.

[7] Hume and Kolthoff, *J. Amer. Chem. Soc.*, 1950, **72**, 4423.

[8] Masaki, *Z. phys. Chem.*, 1932, *A*, **159**, 223.

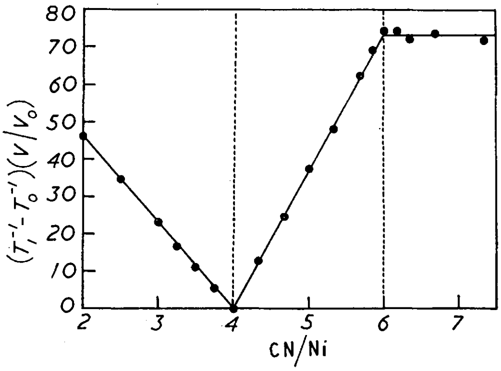
$Ni(NH_3)_6^{2+}$ into $Ni(CN)_4^{2-}$. This is seen to be complete when the ratio CN/Ni is 4. The rectilinear course of the subsequent upward branch indicates that the new relaxing species is formed by a reaction which is also stoicheiometrically complete. The corrected relaxation time decreases until the ratio CN/Ni is 6 and thereafter the only effect of addition of cyanide is that of dilution. The species responsible for relaxation therefore contains six cyanide groups per nickel atom. Since a co-ordination number greater than 6 is improbable, the species will be referred to as $Ni(CN)_6^{4-}$. This conclusion is further confirmed by the rectilinear graph of $(T_1^{-1} - T_0^{-1})$ (after the minimum in Fig. 2) against the concentration of $Ni(CN)_6^{4-}$, calculated on the assumption that each addition of two moles of cyanide will generate quantitatively one mole of $Ni(CN)_6^{4-}$ (Fig. 3).

FIG. 1. *Proton relaxation by* $Ni(NH_3)_6^{2+}$.



Small circles: Measurements on $Ni(NH_3)_6^{2+}$ (ref. 2).
Large circles: Results of Table 2 (cols. 4 and 7).
Dots: Results of Table 1, $[Ni(NH_3)_6^{2+}]$ being taken as $\frac{1}{2}[Ni(CN)_2]$ stoich.

FIG. 2. *Proton relaxation in ammoniacal solutions of* $Ni(CN)_2$ + KCN.



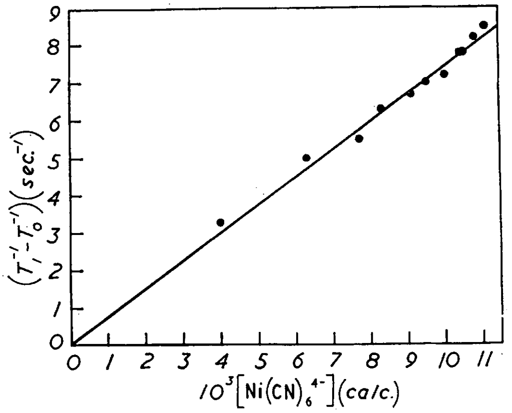


FIG. 3. *Proton relaxation by* $Ni(CN)_6^{4-}$ (*cols.* 5 *and* 7, *Table* 2).

The agreement of all observations with the assumption that tetracyanonickelate(II) and hexacyanonickelate(II) are the only complexes formed between nickel and cyanide under our conditions rules out the occurrence of $Ni(CN)_5^{3-}$ in any significant concentration. The existence of this species has been suggested,[9] and evidence for its occurrence cited.[10]

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[9] Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, 1952, p. 226.

[10] Morris and Nyholm, quoted by Nyholm, *Chem. Rev.*, 1953, **53**, 279.

Spectrophotometric results held to indicate the formation of $Ni(CN)_6^{4-}$ have recently been published.[11]

According to eqn. (1), the slope of the line in Fig. 3 is equal to $\alpha\mu_N^2$, whence it follows that the effective magnetic moment of $Ni(CN)_6^{4-}$ (for proton relaxation in ammoniacal solutions) has a value of 1·58 B.M. This result is to be compared with the value 1·75 B.M. observed for $Ni(NH_3)_6^{2+}$ under the same conditions.[2] Both these values are much lower than the " spin-only " moments, calculated on the assumption of two unpaired electrons. This kind of discrepancy has previously been noted in many cases.[4] It is generally accepted that hexamminenickel(II) has two unpaired electrons and one might thus conclude that the only slightly lower value now found for $Ni(CN)_6^{4-}$ indicates a similar electronic configuration and arrangement of ligands. However, approximate measurements of the susceptibility of aqueous solutions of $K_4Ni(CN)_6$ indicate that the magnetic dipole moment of this species must be very small or zero, and Professor Nyholm has personally informed us that this result has been confirmed in his laboratory. The two sets of measurements are not absolutely comparable since the susceptibility measurements relate to aqueous solutions whereas the relaxation studies concern ammoniacal solutions. Nevertheless, it does not seem likely that the nature of the hexacyano-complex is different in the two cases.

Whilst this observation does not in any way affect the validity of the conclusions concerning cyanide complexes of nickel(II) drawn from the relaxation measurements, it also raises a more important issue. The species $Ni(CN)_6^{4-}$ appears to be highly effective in inducing proton relaxation but seemingly does not do so by virtue of a permanent magnetic dipole moment. This indicates, more convincingly than the recognised discrepancies between magnetic moments deduced from susceptibility measurements and from relaxation measurements,[4] that the relaxation measurements provide some information about molecular structure which is additional to the information obtainable from susceptibility measurements. We are as yet unable to interpret this deduction.

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, April 17th*, 1959.]

[11] Kišová and Čuprová, *Chem. Listy*, 1958, **52**, 1422; see also Cremoux and Mondain-Monval, *Bull. Soc. chim. France*, 1949, 700; cf. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.