[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Exchange Reactions of Tetracyanonickelate Ion: The Structure of Nickel Cyanide[1a]

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The exchange of cyanide between tetracyanonickelate ion and cyanide ion has been studied by a solvent extraction procedure for removing the cyanide as hydrocyanic acid. The exchange is very fast, in agreement with the earlier work of Adamson, Welker and Volpe who used a different separation procedure.

The exchange of nickel between tetracyanonickelate ion and hydrated nickel ion is slow compared to the rate of the precipitation of nickel cyanide which occurs when these ions are mixed. The results lead to the conclusion that solid nickel cyanide contains two non-equivalent kinds of nickel and this is strong evidence that the solid nickel cyanide is really nickel tetracyanonickelate.

The exchange of tetracyanonickelate ion has been studied at room temperature with four complex nickel ions of lower stability: nickel ammonio ion, trisethylenediaminonickelate ion, bisoxalatonickelate ion and the nickel tartrate complex ion. For the two positively charged ions the exchange is very fast but is slowed down to a measurable rate by addition of neutral salt. For the two negatively charged ions the exchange is quite slow but is speeded up considerably by addition of neutral salt. These facts suggest that a direct bimolecular interaction is a plausible mechanism for the exchanges.

Tetracyanonickelate ion is known to be a highly stable complex ion. For example, the nickel cannot be precipitated from the complex by dimethylglyoxime or by sulfide. In view of this stability and the covalent character of the cyanide–nickel bonds as shown by magnetic susceptibility,[2] one might expect the exchange reactions of the complex ion with isotopically labeled nickel or cyanide ions to be slow. Actually, Adamson, Welker and Volpe[3] have reported that the exchange of cyanides between tetracyanonickelate ion and cyanide ion in solution is immeasurably fast. To gain further information on the properties of this complex ion we have studied the exchange of the nickel in tetracyanonickelate ion with (hydrated) nickel ion. One of the results of this work is information on the structure of solid nickel cyanide. A few experiments have also been made on the cyanide ion–tetracyanonickelate ion exchange using a different separation procedure from that of Adamson, Welker and Volpe. Finally we have studied the exchange of nickel in tetracyanonickelate ion with the nickel of several nickel complex ions of lower stability.

Experimental Procedures

The Ni^{63} used in the exchange studies was obtained from Oak Ridge as nickel metal. It was dissolved in acid and freed from radioactive contaminants by successive precipitations with dimethylglyoxime from solutions to which carrier amounts of iron and cobalt had been added. Since the radiation from Ni^{63} is very soft (0.05 mev. β^-) the radioactivity was determined in a windowless, flow-type counter. For about half of the experiments the nickel was counted as the dimethylglyoxime precipitate; for the others the nickel was plated out on copper. In both cases the samples were "infinitely thick," *i.e.*, thicker than the maximum range of the beta particles, so that the relative specific activity of the sample was given directly by the count. The per cent. exchange is then given by 100 times the ratio of specific activity at a given time to that at isotopic equilibrium. Due to uncertainties in both sample preparation and actual counting the per cent. exchange figures probably have a standard deviation of about 5%.

The separation of nickel ion, free or complexed, from tetracyanonickelate ion was done in all experiments by precipitation with dimethylglyoxime at *p*H values of from 5 to 8. All exchange experiments were made at room temperature, 23 ± 2°.

The chemicals used met accepted standards for purity. Some of the solutions of potassium tetracyanonickelate were prepared from the calculated amounts of nickel chloride and potassium cyanide solutions; others were prepared directly from recrystallized potassium tetracyanonickelate and concentrations determined by nickel analysis. Solid trisethylenediamine nickel chloride was prepared by the method of Werner[4] followed by recrystallization from water.

The Ni^{++}-$Ni(CN)_4^=$ Exchange.—A study of this exchange is complicated by the fact that even in solutions of *p*H 1 or 2 a mixture of nickelous ion and tetracyanonickelate ion gives almost quantitatively a finely divided precipitate of nickel cyanide. However, it was found experimentally that if excess dimethylglyoxime solution is added to the suspended precipitate the latter is quantitatively transformed into tetracyanonickelate ion and a precipitate of nickel dimethylglyoxime, *i.e.*, only an amount of nickel equal to that added to the complex ion solution is precipitated. This quantitative separation makes it possible to study the amount of exchange which occurs before or during the precipitation of the nickel cyanide.

For all the exchange experiments with this system solutions of radioactive nickel chloride were mixed with solutions of potassium tetracyanonickelate and to the resulting suspension of nickel cyanide excess dimethylglyoxime and either a hot ammonia buffer solution or a hot acetate buffer solution was added, and the resulting precipitate was filtered off. The *p*H of the original mixture was adjusted by adding either hydrochloric acid or small amounts of phthalate buffers.

The $Ni(CN)_4^=$-CN^- Exchange.—This exchange was studied using sodium cyanide containing radioactive C^{14}. Since it was desired to employ a different type of separation technique than that used by Adamson, Welker and Volpe, it was decided to try separation of hydrocyanic acid by partition. The partition ratio of hydrocyanic acid between diethyl ether and water is $C_{et}/C_w = 2.4$[5] which makes quantitative extraction of HCN relatively easy. The final procedure to give a rapid and fairly complete separation of the cyanide was as follows. A 10-ml. sample of the exchange mixture was added to a separatory flask containing 100 ml. of ether and 5 ml. of a 0.2 molar potassium hydrogen phosphate, 0.2 molar potassium dihydrogen phosphate buffer solution (*p*H 6.5). The mixture was quickly shaken, the aqueous layer drawn off and the ether layer transferred to another separatory funnel where it was extracted with three 6-ml. portions of 0.1 molar sodium hydroxide. Preliminary tests showed that somewhat over 90% of the original cyanide was recovered by this procedure and also that tetracyanonickelate was not extracted in detectable quantities. The relatively high *p*H used in the separation as well as the rapidity of the operation decreases the possibility of induced exchange caused by the separation technique.

The cyanide in the final solution was recovered by adding 10 ml. of a 2 molar sodium acetate, 1 molar acetic acid buffer solution followed by 5 ml. of 0.1 molar silver nitrate. The resulting silver cyanide was filtered onto a flat filter paper which in turn was mounted on a metal disc for count-

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(1) (a) Work done at the Brookhaven National Laboratory, Upton, N. Y., under the auspices of the Atomic Energy Commission. (b) Permanent address: Department of Chemistry, Cornell University, Ithaca, N. Y.

(2) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 111.

(3) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL **72**, 4030 (1950).

(4) Werner, *Z. anorg. Chem.*, **21**, 201 (1899).

(5) Deniges, *Bull. trav. soc. pharm., Bordeaux*, **78**, 61 (1940).

ing. The final samples for counting were essentially infinitely thick.

The $Ni(NH_3)_x^{++}$-$Ni(CN)_4^{=}$ Exchange.—In all cases the complex ammonio ion was prepared by adding excess ammonia solution or ammonia–ammonium ion buffer solution to radioactive nickel chloride. To this mixture the solution of potassium tetracyanonickelate was added and the nickel from the ammonio complex later precipitated with excess dimethylglyoxime with a subsequent addition of hot water or hot potassium acetate solution to coagulate the dimethylglyoxime precipitate. Separate experiments showed the separation is quantitative.

The $Ni(en)_3^{++}$-$Ni(CN)_4^{=}$ Exchange.—For one set of experiments the radioactivity was in the ethylenediamine complex ion; for the other it was in the cyanide complex ion. For the former the ethylenediamine complex was prepared by mixing the calculated amounts of standardized ethylenediamine and radioactive nickel chloride solutions. For the other set of experiments solutions of the ethylenediamine complex were prepared from solid trisethylenediamine nickel chloride and the solution of radioactive tetracyanonickelate ion was prepared from the calculated amounts of sodium cyanide and radioactive nickel chloride. The separation procedures were very similar to those discussed in the previous section.

The $Ni(Ox)_2^{=}$-$Ni(CN)_4^{=}$ Exchange.—Definite information on the formula of the nickel oxalate complex ion in solution is apparently not available although the solid salt $K_2Ni(Ox)_2$ is known. One of the undoubted difficulties is that a solution of bisoxalatonickelate ion is unstable and partially transforms into a precipitate of nickel oxalate. Other evidence (precipitation with dimethylglyoxime, decomposition by ammonia, etc.) indicates the complex ion is of relatively low stability. Specifically, a solution of this complex when mixed with a solution of tetracyanonickelate ion gives a precipitate unless excess oxalate ion is present. Consequently all exchange studies were made with excess oxalate. Separation was done by precipitation with dimethylglyoxime at a *p*H of about 6.

The $Ni(CN)_4^{=}$-$Ni(Tartrate)^-$ Exchange.—The nickel tartrate complex ion is moderately stable in neutral solutions and is apparently considerably more stable in basic solutions. Bobtelsky and Jordan[6] who have made an extensive study of this complex report that the complex involves a one to one ratio of nickel and tartrate ions. The complex is a fairly strong acid, presumably due to ionization of a proton from one of the hydroxyl groups, so that in basic solution the formula appears to be $NiTr^-$. (We have some indication that in basic solutions the complex may involve two tartrates to each nickel but this needs more investigation.)

In the majority of the exchange studies the complex ion solutions were prepared with two moles of tartrate to one of radioactive nickel ion and usually also with added base. These solutions were then mixed with solutions of tetracyanonickelate ion, samples removed at stated times and the nickel from the tartrate complex precipitated with dimethylglyoxime at a *p*H of around 8 or 9.

Results and Discussion

The Ni^{++}-$Ni(CN)_4^{=}$ Exchange.—The complication in a study of this exchange caused by precipitation of nickel cyanide has been discussed previously. Actually this difficulty makes it possible to gain an added item of interesting information, namely, information on the structure of nickel cyanide. Feigel, Demant and de Oliveira,[7] on the basis of precipitation reactions, have suggested that solid nickel cyanide has the structure $NiNi(CN)_4$. Assuming this, the following reactions would explain our precipitation and separation results

$$Ni^{++} + Ni(CN)_4^{=} = NiNi(CN)_4$$
$$NiNi(CN)_4 + 2HDMG = Ni(DMG)_2 + Ni(CN)_4^{=} + 2H^+$$

where HDMG refers to dimethylglyoxime.

If, as postulated here, there are two non-equivalent kinds of nickel in solid nickel cyanide and, further, if the exchange of nickel between nickel ion and the cyanide complex ion is slow, then the nickel in the final dimethylglyoxime precipitate should come entirely from the added nickel salt and not from the nickel in the complex ion.

The experimental results on this exchange are given in Table I. At *p*H values of from 4 to 8 there is no exchange within the limit of error. This is true if either excess nickel ion or complex ion is present. These results lead to two conclusions. First, the exchange of nickel between the free and complexed ions is slow compared to the speed of precipitation of nickel cyanide. Second, solid nickel cyanide contains non-equivalent nickels. About the only reasonable explanation for this last is that the solid salt is really nickel tetracyanonickelate, *i. e.*, that the equations above properly describe the precipitation and separation.

TABLE I

EXCHANGE BETWEEN Ni^{*++} AND $Ni(CN)_4^{=}$ AT 23° IONIC STRENGTH 0.1 OR LOWER

t is time between mixing solutions and adding dimethylglyoxime

Concn. Ni^{*++}, *M*	Concn. $Ni(CN)_4^{=}$, *M*	*p*H	*t*, min.	Exchange, %
0.0067	0.0067	8.0	1	6
.0067	.0067	4.2	1	−4
.0067	.0096	4.2	1	1
.0067	.0040	4.2	1	0
.0067	.0067	1.5	1	29
.0067	.0067	1.5	1	32
.0067	.0067	1.5	32	30
.0067	.0067	1.5	180	39

At a *p*H of 1.5 (0.04 molar hydrochloric acid) there is a partial exchange of nickel, the degree of which does not increase with an increase in time between initial mixing and addition of dimethylglyoxime. This last fact indicates that the exchange occurs before the precipitation of the nickel cyanide which, of course, occurs immediately after mixing. This increased exchange at low *p*H is doubtless connected with an increase in the rate or extent of dissociation of the cyanide complex.

The CN^--$Ni(CN)_4^{=}$ Exchange.—Experiments on this exchange were run at an ionic strength of 0.1 with concentrations of 0.02 molar cyanide ion and 0.005 molar complex ion. The *p*H values ranged from 6.5 to 10.5. For all experiments the exchange was complete within one-half minute. This very fast exchange using an extraction procedure for separation agrees with the work of Adamson, Welker and Volpe whose separation procedure involved precipitation.

The $Ni(NH_3)_x^{++}$-$Ni(CN)_4^{=}$ Exchange.—Johnson and Hall,[8] who studied several exchange reactions between radioactive nickel ion and complex ions of nickel, reported that in one or two cases addition of ammonia to their solutions before precipitation of the nickel with dimethylglyoxime induced a rapid exchange which was not found when other separation schemes were used. We have found this same effect in some of our studies and it sug-

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(6) Bobtelsky and Jordan, THIS JOURNAL, **67**, 1828 (1945).

(7) Feigel, Demant and de Oliveira, *Anais Asso. Quim. do Brasil*, **3**, 72 (1944).

(8) Johnson and Hall, THIS JOURNAL, **70**, 2344 (1948).

gested that exchange reactions involving the nickel ammonia complex might be considerably faster than those of the hydrated nickel ion.

As was pointed out by Bjerrum in his extensive investigation,[9] the composition of the nickel ammonio complex is variable and its stability is relatively low. Due to this low stability a mixture of the nickel ammonio complex ion and tetracyanonickelate ion gives a precipitate of nickel cyanide unless a considerable (*ca.* 0.3 molar) excess of ammonia is present. Because of this, all exchange experiments were made using solutions which contained excess ammonia.

Experiments using 0.005 molar concentration of the two complex ions and 0.3 molar ammonia gave complete exchange within 0.4 minute. Clearly the exchange of the cyanide complex with the complex ammonio ion is very fast, in contrast to the result with hydrated nickel ions. Rather interestingly the exchange for solutions of these same concentrations but with 4.4 molar ammonium nitrate also present is measurably slow; in two experiments the amount of exchange was 76 and 79% in 0.4 minute. This decrease in rate of exchange with added salt is to be expected if the slow step is a reaction between oppositely charged ions; in particular the decrease is consistent with a rate-determining bimolecular reaction between the two oppositely charged complex ions.

The $Ni(en)_3^{++}$–$Ni(CN)_4^{=}$ Exchange.—Although trisethylenediaminonickelate ion is precipitated by dimethylglyoxime, it is sufficiently stable so that mixtures of this complex and tetracyanonickelate ion do not give a nickel cyanide precipitate. This is consistent with the high stability of the ethylenediamine complex reported by Bjerrum.[9] However, Johnson and Hall[8] have reported that the exchange between radioactive nickel ion and nickel in the ethylenediamine complex is immeasurably fast. Thus a comparison between the exchange of nickel in the ethylenediamine complex with the cyanide complex and the analogous exchange involving the nickel ammonio complex should be of some interest. Information on the former exchange is given in Table II.

TABLE II

EXCHANGE BETWEEN $Ni(en)_3^{++}$ AND $Ni(CN)_4^{=}$ AT 23°

Concn. $Ni^*(en)_3Cl_2$ and $K_2Ni(CN)_4$, *M*	Concn. other	*p*H	*t*, min.	Exch., %
0.005	0.01 *M* KCl	10.6	0.5	101
.005	....	10.0	.75	92
.005	.030 *M* en	10.9	.75	99
.005	.02 *M* KH_2PO_4	7.1		
	.02 *M* K_2HPO_4		(a) .6	71
			(b) 1.6	82
			(c) 10.0	97
.005	3 *M* $NaClO_4$	9.5	0.8	51
.005	3.3 *M* $NaClO_4$	10.2	1.2	44

At *p*H 9 to 11 the exchange is immeasurably fast. Excess ethylenediamine causes no measurable decrease in rate. When the *p*H is decreased from 9 to 7 the rate of exchange is slowed down enough to be just measurable. At the lower *p*H the ethylenediamine complex is considerably decomposed[9] and of course the nickel ion concentration greatly increased. The observed decrease in rate of exchange with increasing acidity indicates that a mechanism involving dissociation of the ethylenediamine complex does not enter.

The final two entries of Table II are of considerable interest since this decrease in rate with added neutral salt is similar to the decrease obtained with the analogous ammonia exchange. From these and other experiments not listed the half-time for the exchange with 0.005 molar complex ion and 3 molar sodium perchlorate is approximately one minute. Without the added salt the half-time for exchange appears to be not over 0.1 minute. There is thus at least an order of magnitude decrease in rate of exchange caused by the sodium perchlorate. This large salt effect again suggests that a direct bimolecular reaction between the oppositely charged complex ions is a likely mechanism for the exchange.

The $Ni(Ox)_2^{=}$–$Ni(CN)_4^{=}$ Exchange.—It is clear from Table III, which gives the experimental results for this exchange, that at high *p*H the exchange of nickel between these two complex ions is quite slow in striking contrast to the results for the two previous cases. At rather low *p*H values the exchange is somewhat faster; this is probably due to dissociation of the tetracyanonickelate ion.

TABLE III

EXCHANGE AT 23° BETWEEN $Ni^*(Ox)_2^{=}$ AND $Ni(CN)_4^{=}$

Concn. $Ni^*(Ox)_2^{=}$ and $Ni(CN)_4^{=}$, *M*	Concn. other	*p*H[a]	*t*, min.	Exch., %
0.0067	0.0068 *M* K_2Ox; .0133 *M* KCl	8	9	5
.0067	.0068 *M* K_2Ox; .0133 *M* KCl	6	3	0
	No buffer			
.0067	.0068 *M* K_2Ox .0133 *M* KCl	4.2	11	16
.005	.005 *M* K_2Ox:	4.2		
	.025 *M* KCl		(a) 1.3	0
			(b) 163	44
.005	.005 *M* Na_2Ox	7.1		
			(a) 60	3
			(b) 154	16
.005	.005 *M* Na_2Ox	6.7		
	2.9 *M* $NaClO_4$		(a) 60	24
			(b) 159	36

[a] Unless otherwise noted, *p*H established by low concentrations of either phosphate or phthalate buffers.

The last two entries of Table III show the influence of large amounts of neutral salt on this exchange. The presence of 2.9 molar sodium perchlorate increases the rate of exchange by a factor of two or three. The direction of the effect is that predicted for a reaction between similarly charged ions but the magnitude seems somewhat small for a primary salt effect.

The $Ni(CN)_4^{=}$–Ni(Tartrate)$^{-}$ Exchange.—Table IV gives the experimental results. At *p*H values of from 7 to 10 the exchange is quite slow, a result which is similar to that obtained with the oxalate complex. The data at a *p*H

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[9] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1941.

value of 10 for 0.005 molar concentrations of the complex ions and with low salt concentration lead to a rough value of 2800 minutes for the half-time of the exchange. The final entries in the table show that, just as for the oxalate case, the rate of exchange is increased by neutral salt; the half-time in the presence of 2.4 molar sodium perchlorate is approximately 300 minutes.

TABLE IV

EXCHANGE AT 23° BETWEEN $Ni(CN)_4^=$ AND $Ni^*(Tr)^-$

Concn. of $Ni(Tr)^-$ and $Ni(CN)_4^=$, *M*	Concn. other	*p*H	*t*, min.	Exch., %
0.005	0.005 *M* KOH	9.7	6	1
	.01 *M* K_2Tr			
.005	.005 *M* KOH	10.2		
	.01 *M* K_2Tr		(a) 25	0
			(b) 981	22
			(c) 40100	62
.005	.005 *M* NaOH	10.3		
	.01 *M* Na_2Tr		(a) 30	11
	2.4 *M* $NaClO_4$		(b) 154	27

The over-all picture of the exchange of nickel between tetracyanonickelate ion and other complex ions containing nickel is surprisingly consistent. There is no indication that the extent of dissociation of the second complex ion is of much importance. Otherwise one might expect larger differences than observed between complexes of the same charge and one might have expected the exchange listed in Table IV involving the ethylenediamine complex and excess ethylenediamine to be relatively slower. In contrast the charge of the second complex ion appears to be quite significant. Exchanges between complex ions of the same sign are slow; those between ions of opposite charge are fast. The slow rate of exchange between the tetracyanonickelate ion and free nickel ion constitutes an apparent exception to this last statement. However this experiment actually involves a competitive process; the only definite conclusion is that the rate of exchange is slow compared to the rate of precipitation of nickel cyanide and the latter may well be very fast.

The fact that added salt slows down the exchanges between complex ions of opposite charge and speeds up those with similar charge makes a direct bimolecular exchange process a plausible one. The comparative independence of rate of exchange on stability of the complex ions also suggests this mechanism. However a more detailed kinetic investigation is needed to settle this point.

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Cyanoalkylation. III. Structural Effects in the Reaction of Mercaptans with α-Alkylacrylonitriles

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The conjugate addition of mercaptans to α-alkylacrylonitriles has been investigated. In the presence of a piperidine–mercaptan salt catalyst, primary, tertiary and aromatic mercaptans have been added to α-methylacrylonitrile, α-ethylacrylonitrile, α-isopropylacrylonitrile and α-*n*-amylacrylonitrile. Of the mercaptans examined as addenda, thiophenol afforded the best results and rather poor reaction was realized with *t*-butyl mercaptan. The nature of the alkyl group, situated on the alpha carbon atom of the nitrile, appeared to have little, if any, effect upon the ease with which conjugate addition took place.

Previous communications[1,2] from this Laboratory have revealed that catalysts of the piperidine-salt type are effective in promoting the conjugate addition of certain mercaptans to β-alkylacrylonitriles and 1-cyano-1-cyclohexene. The present investigation was undertaken primarily to determine whether or not these catalysts would be equally efficient in causing satisfactory addition of mercaptans to α-alkylacrylonitriles. As a direct result of the program, a secondary objective was resolved into a study of the effects of mercaptan and nitrile structure upon the course of reaction.

Primary, tertiary and aromatic mercaptans were found to be cyanoalkylated with α-methylacrylonitrile, α-ethylacrylonitrile, α-isopropylacrylonitrile and α-*n*-amylacrylonitrile provided that a piperidine–mercaptan salt was employed as a catalyst in the reaction. Data for the additions are incorporated in Table I.

Use of the salt as a catalyst was particularly rewarding in the cases of the aromatic and primary mercaptans, wherein the corresponding adducts were isolated in yields which ranged from 60–99%. Thiophenol appeared to be the most active agent within the group of mercaptans studied. On the other hand, it is recognized that the differences in reactivity of thiophenol and benzyl mercaptan, as was adjudged by the quantities of adducts produced, were not marked.

The poorest results were realized when *t*-butyl mercaptan was employed as the addendum. Because steric factors were not considered to play prominently in conjugate additions of this nature, the slight nucleophilic activity of *t*-butyl mercaptan was held responsible[3] for the unsatisfactory reaction.

When the mercaptan, bis-(2-mercaptoethyl) sulfide, was dicyanoalkylated with α-methylacrylonitrile, an interesting tris-thio ether was isolated in surprisingly good yields. The adduct proved to be thermally stable at its boiling point of 225° (0.1 mm.).

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[1] R. M. Ross, THIS JOURNAL, **71**, 3458 (1949).

[2] R. M. Ross and F. W. Raths, *ibid.*, **73**, 129 (1951).

[3] For other examples of conjugate additions of a similar type which are not affected greatly by bulky groups, see references 1 and 2, and R. C. Fuson and H. L. Jackson, *ibid.*, **72**, 1637 (1950).