with the determinations by electron diffraction of Wierl[12] (2.38 ± 0.08 Å.) and Maxwell, Mosley, and Deming[13] (2.38 ± 0.05 Å.), and with the length predicted from the moment of inertia[14] (2.31 Å.). The structure found for hydrogen azide is identical with that proposed by Eyster[15] from a consideration of the moments of inertia, and on the assumption that the resonating structures are chiefly I + II.

Summary

The structures of nitrous oxide and hydrogen

(12) R. Wierl, *Physik. Z.*, **31**, 1028 (1930).
(13) L. Maxwell, V. Mosley and L. Deming, *J. Chem. Phys.*, **2**, 331 (1934).
(14) E. F. Barker, *Phys. Rev.*, **41**, 369 (1932).
(15) E. H. Eyster, *J. Chem. Phys.*, **8**, 141 (1940).

azide have been investigated by the electron diffraction method.

For nitrous oxide $r_1 + r_2 = 2.32 \pm 0.02$ Å., and $0.925 < r_1/r_2 < 1.08$. The distances $r_1 = 1.12$ Å. and $r_2 = 1.19$ Å. predicted by Pauling on the basis of his adjacent charge rule give a ratio, 0.94, which lies between these limits. It is shown that the distances found by the use of Badger's rule also have the ratio 0.94.

For hydrogen azide the distances found are $r_3 = 1.13_6 \pm 0.01$ Å. and $r_4 = 1.24_7 \pm 0.01$ Å., on the basis of an assumed linear N_3 group. The report of Eyster, made on the basis of his values of the moments of inertia and Pauling's adjacent charge rule, is confirmed. It is shown that the application of Badger's rule yields similar results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solutions. VII. The Reduction of Complex Nickel Cyanides: Mono-valent Nickel

BY JOHN W. EASTES AND WAYLAND M. BURGESS[1]

The red color produced by the reduction of aqueous solutions of potassium cyanonickelate, $K_2Ni(CN)_4$, was shown by Bellucci and Corelli[2] to be attributable to a substance having the empirical formula $K_2Ni(CN)_3$. This substance had, however, never been isolated.

In the course of a study of the reduction of nickel salts in anhydrous liquid ammonia,[3] $K_2Ni(CN)_3$ was observed to be formed and we have now succeeded in isolating it in a pure condition, both from solutions of liquid ammonia and from aqueous solutions, and subjecting it to a complete analysis and study.

Materials Used

Alkali Metals.—Kahlbaum metallic sodium and potassium were used. The sodium was analyzed by solution in 95% ethanol, conversion to sodium chloride by the addition of excess hydrochloric acid, evaporation to dryness and weighing as sodium chloride. An average of four analyses gave a value of 100.5% sodium, with a maximum deviation of 0.2%. The potassium was analyzed in a

similar manner, but with the addition that it was also precipitated and weighed as $K_2NaCo(NO_2) \cdot 6H_2O$[4] and found to be 100.4% potassium, with a maximum deviation of 0.4%.

Sodium and Potassium Cyanonickelate; $Na_2Ni(CN)_4$, $K_2Ni(CN)_4$.—These two compounds were prepared in a pure form by recrystallization of the product obtained by concentrating a dilute solution formed by dissolving freshly precipitated nickel cyanide in a solution of the alkali metal cyanide. The anhydrous products had the analyses: for $Na_2Ni(CN)_4$—28.07% Ni (calcd. 28.12% Ni), 49.93% CN (calcd. 49.85% CN); for $K_2Ni(CN)_4$—24.30% Ni (calcd. 24.36% Ni), 43.56% CN (calcd. 43.18% CN).

Preparation of $K_2Ni(CN)_3$ in Liquid Ammonia.—Reactions in anhydrous liquid ammonia were carried out as described by Burgess and Eastes,[3] a diagram of the apparatus used being shown in Fig. 1.

By the reaction of *excess* potassium cyanonickelate with sodium or potassium, $K_2Ni(CN)_3$ was prepared in liquid ammonia solution as follows. The reaction tube was two-thirds filled with anhydrous liquid ammonia, which was then saturated with potassium cyanonickelate. To this solution was added a small piece, approximately 0.1 g., of sodium or potassium. A bright red, dense precipitate slowly formed in the solution and settled out at once. No hydrogen was formed during the reaction. When the alkali metal had all reacted, the yellow solution above the red precipitate was siphoned off and the red precipitate

(1) This article is based upon the thesis presented to the Faculty of the Graduate School of the University of Cincinnati by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy. 1936. No. VI. THIS JOURNAL, **63**, 2674 (1941).
(2) Bellucci and Corelli, *Z. anorg. Chem.*, **86**, 88–104 (1914).
(3) Burgess and Eastes, THIS JOURNAL, **63**, 2674–6 (1941).
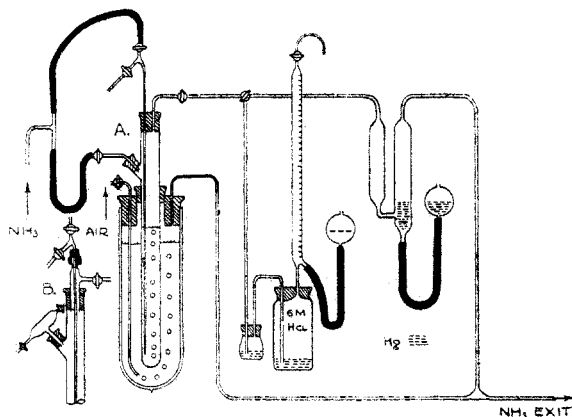(4) Hamid, *Analyst*, **51**, 450 (1926).

Fig. 1.—Apparatus for carrying out reactions in anhydrous liquid ammonia at its boiling point. A, arrangement of reaction tube fittings for addition of alkali metals, and salts to solutions; B, arrangement of reaction tube fitting for washing precipitate with liquid ammonia and collecting samples of products.

washed several times with anhydrous liquid ammonia. Finally, the remaining liquid ammonia was evaporated from the reaction tube at room temperature and pressure, after which the red powder was shaken into the sample tube, Fig. I-B, and sealed off with with the hand torch. The remaining ammonia was removed from the sample tube by gentle suction and then the tube was swept out with dry, oxygen-free nitrogen previous to weighing.

Samples prepared in this way were analyzed by first dissolving in water, in which they gave deep red solutions, and analyzing these solutions for nickel (dimethylglyoxime), cyanide (Volhard), and potassium (sodium cobaltinitrite). Typical analyses are given in Table I, which shows the product to be definitely $K_2Ni(CN)_3$, potassium cyanonickelite.

TABLE I

ANALYSES OF $K_2Ni(CN)_3$

Sample, g.	% Sample accounted for[b]	Alkali metal used	Atomic ratio		
			K	Ni[a]	CN
Prepared in Liquid Ammonia Solution					
0.5301	99.01	K	2.137	1.000	3.057
.7651	. . .	Na	2.000	1.000	2.887
.8903	. . .	Na	2.000	1.000	2.985
Prepared in Aqueous Solutions					
0.1762	95.35	K	1.903	1.000	2.838
.0863	99.15	K	1.702	1.000	2.974
.2306	99.90	K	2.029	1.000	2.986
.1456	96.45	K	1.993	1.000	2.955
.1345	98.90	K	1.994	1.000	2.787
.3465	98.75	Na	2.027	1.000	3.030

[a] The value of unity is assumed for nickel. [b] The sum of the analyses for nickel, cyanide and potassium.

Properties of $K_2Ni(CN)_3$.—Potassium cyanonickelite is a bright red solid of amorphous appearance. Samples exposed to the air retain their initial appearance for about an hour, after which it becomes apparent that a transformation to a yellow material is taking place. It dissolves

in water without decomposition to give blood red solutions the intensity of the color depending upon the concentration. On standing in air these red solutions gradually change color, finally becoming yellow. This color change is attended by the precipitation of nickel hydroxide and an increase in the alkalinity of the solution. This same color change is easily brought about by such oxidizing agents as hydrogen peroxide, and iodine solution. When such oxidizing agents are used, no nickel hydroxide precipitates.

On standing in a closed system, aqueous solutions of $K_2Ni(CN)_3$ very slowly lose their red color, hydrogen gas being evolved during the discoloration. Aqueous solutions of $K_2Ni(CN)_3$ instantly reduce solutions of silver nitrate and gold chloride, giving precipitates of silver and gold.

The above properties of $K_2Ni(CN)_3$ make it evident that it is the compound responsible for the red solutions produced when aqueous solutions of $K_2Ni(CN)_4$ are reduced.

Isolation of $K_2Ni(CN)_3$ from Aqueous Solution.—Approximately 20 ml. of a saturated aqueous solution of $K_2Ni(CN)_4$ was placed in a test-tube fitted with a stopcock at the bottom and a closed side arm attached in the middle at a 45° angle downward. To this was added 5 ml. of a potassium (or sodium) amalgam, a stopper put in place at once and the mixture shaken, with thumb holding the stopper in place. The evolved hydrogen was vented through the stopcock (thus, an atmosphere of hydrogen was maintained in the apparatus). When the amalgam became exhausted, the mercury was collected in the side arm and the bright red solution run from the apparatus through the stopcock into the liquid ammonia reaction tube (Fig. 1) which contained 100 ml. of 95% ethanol, agitated with hydrogen gas. Slow introduction of this red aqueous solution *into the alcohol* caused the formation of a bright red solid precipitate (not an oil). This dense red solid settled out at once when the agitation was stopped leaving a pale yellow solution above. It was washed three times with alcohol by decantation in the same manner that precipitates are washed with liquid ammonia, hydrogen gas being used to supply the pressure to force the alcohol out of the reaction tube and for agitation. Then the precipitate was washed five times with liquid ammonia to free it of $K_2Ni(CN)_4$, KCN, etc. Thereafter, the bright red precipitate was treated as described in the preceding section.

It had all the properties described above for $K_2Ni(CN)_3$ prepared in liquid ammonia and analyses of samples (Table I) showed it to be $K_2Ni(CN)_3$. Thus, the same compound has been prepared in and isolated in a pure form from both aqueous and liquid ammonia solutions.

Preparation of $M_2^INi(CN)_4$.—In order to prepare $K_2Ni(CN)_3$ in liquid ammonia, an *excess of potassium cyanonickelate* was allowed to react with the alkali metal. When the *alkali metal is in excess*, a reaction of different character takes place. It proceeds as follows.

The clump of alkali metal floated around in the solution, sometimes breaking into smaller pieces. At the surface of the alkali metal, reaction could be seen slowly taking place, a bright red precipitate being formed. As the reaction proceeded the alkali metal was used up and the volume of precipitate increased until finally the bulky precipitate

seemed to gell in the solution. Shortly thereafter the solution became blue due to solution of the excess alkali metal. Up to this point no gas was evolved from the reaction, but thereafter pure hydrogen was evolved slowly until the excess alkali metal (blue color) disappeared. There remained a *bulky yellow* precipitate.

These yellow precipitates were prepared for analysis by first washing ten times with liquid ammonia. The washed precipitate was then freed of liquid ammonia by evaporation, swept with dry, oxygen-free nitrogen and sealed off in the sample tube (Fig. 1-B) by use of the hand torch.

Table II shows the relationship between the amount of alkali metal and alkali metal cyanonickelate used and Table III gives analyses of the reaction product, the yellow precipitate.

TABLE II

REACTION RATIOS OF ALKALI METAL AND ALKALI METAL CYANONICKELATE

Alkali metal used		$M_2^INi(CN)_4$		Found H_2,	Ratio of $M_2^I:M_2^INi-(CN)_4$ (cor.
Metal	Grams	Salt	G.	cc.	for H_2)
K	0.1813	$K_2Ni(CN)_4$	0.4222	12.2	2.03
K	.1466	$K_2Ni(CN)_4$	.4095	39.4	2.00
Na	.1695	$K_2Ni(CN)_4$	.3660	48.5	2.01
Na	.0938	$K_2Ni(CN)_4$	.3050	17.4	2.02
Na	.2115	$Na_2Ni(CN)_4$	.7317	23.7	2.02
Na	.2844	$Na_2Ni(CN)_4$	.5542	80.1	1.97
Na	.1026	$Na_2Ni(CN)_4$	.3185	15.6	2.03
K	.2316	$Na_2Ni(CN)_4$	.5854	3.9	1.99
K	.2122	$Na_2Ni(CN)_4$	.3221	26.4	1.99
K	.1304	$Na_2Ni(CN)_4$	.2552	10.6	1.99

TABLE III

ANALYSES OF $K_4Ni(CN)_4$

Alkali metal	$M_2^INi(CN)_4$ used	% Sample accounted for[b]	Atomic ratio in product		
			K	Ni[a]	CN
K	$K_2Ni(CN)_4$	96.73	3.959	1.000	3.888
K	$K_2Ni(CN)_4$	95.35	3.897	1.000	3.903
K	$K_2Ni(CN)_4$	96.15	4.014	1.000	3.811
K	$K_2Ni(CN)_4$	94.34	3.992	1.000	3.850
K	$K_2Ni(CN)_4$	94.35	4.000	1.000	3.890
K	$K_2Ni(CN)_4$	94.15	3.999	1.000	3.839

[a] The value of unity is assumed for nickel. [b] The sum of the analyses for nickel, cyanide and potassium.

The data show that one gram mole of alkali metal cyanonickelate reacted with two gram atoms of alkali metal to give a product, the yellow precipitate, whose empirical formula may be represented by $M_4^INi(CN)_4$.

This unusual product had the following prop-

erties which distinguished it from $M_2^INi(CN)_3$ whose properties are described above.

As formed in liquid ammonia it was a bulky yellow precipitate, but when freed of ammonia it was an amorphous copper colored solid. This copper colored solid was extremely unstable in air or oxygen, instantly turning black on exposure. It readily dissolved in water, forming a deep red basic solution and simultaneously giving off hydrogen gas. The red solution had all the properties of a solution of $M_2^INi(CN)_3$.

Due to their rapid oxidation in air, samples of $M_4^INi(CN)_4$ were prepared for analysis by dissolving them in boiled distilled water which was drawn into the sample tube to avoid contact of the sample with air. But even then the samples were observed to sometimes "char" slightly. Perhaps this was due to oxidation by the water itself.

Attempts to prepare $M_4^INi(CN)_4$ by the action of alkali metals on $M_2^INi(CN)_3$ in liquid ammonia solution were unsuccessful.

Summary

Solutions of alkali metals in anhydrous liquid ammonia do not react with alkali metal cyanonickelates to give metallic nickel as do (3) the simple nickel salts. Instead reduction products of the alkali metal cyanonickelate are formed in which nickel appears to have a valence of less than two.

An excess of alkali metal reacts on an alkali metal cyanonickelate in anhydrous liquid ammonia to give a product having the empirical formula, $M_4^INi(CN)_4$. No explanation of the state of valence of nickel in this product is offered.

An excess of alkali metal cyanonickelate reacts with an alkali metal in anhydrous liquid ammonia to give a compound of empirical formula $M_2^INi(CN)_3$ in which nickel appears to be monovalent. This compound has been prepared in and isolated pure from both anhydrous liquid ammonia and aqueous solution and is shown to be the compound responsible for the red color produced by the action of reducing agents on aqueous solutions of alkali metal cyanonickelates.