

# Investigation of Preparation, Solubility and Stability Properties of Nickel Hydrazine Nitrate (NiHN)

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**Abstract:** Following an initial, brief, review of the environmental problems associated with the use of lead based primers, and also some of their potential replacements, this study investigated the preparation of the promising, lead free, energetic material nickel hydrazine nitrate by different methods. All three methods trialed produced the same, analytically indistinguishable, compound but with minor changes in visual appearance. The solution properties governing the precipitation process were investigated in a controlled pH titration experiment. Product solubility in a number of common solvents was investigated. Aqueous ammonia and hydrazine hydrate proved the best “non-destructive solvents” for the solid. UV spectroscopy and con-

ductivity of the solutions obtained was used as an indicator of the processes involved in the solubility. Using the critical pH conditions for precipitation from aqueous solutions of hydrazine and nickel nitrate the formation constant for the tris hydrazine complex was determined. Also using the solubility of the tris-hydrazine complex in concentrated hydrazine hydrate an equilibrium constant for the formation of the soluble hexa-hydrazine complex from insoluble tris hydrazine complex was determined. These values were compared with similar values for nickel hydrazine complexes with other anions. The origins of these differences were discussed. Further work on controlling and measuring the particle size of the NiHN produced should be considered.

**Keywords:**

## 1 Introduction

Lead based primary explosives, lead styphnate and lead azide, are widely used in energetic systems because they are comparatively cheap, reliable and effective. The azide is principally used in missile warheads and demolition charges, since it invariably burns to detonation except under very unusual conditions [1]. Lead based initiators are sensitive to a number of accidental stimuli making synthesis, processing, storage and transport extremely hazardous. Azides are more toxic than cyanide [2]. Lead is toxic and has a cumulative effect on both humans and the environment alike. Measurements have shown unacceptable levels of lead particulates in the enclosed conditions in armoured vehicles firing heavy caliber machine guns [3]. More recently the long-term effects of continuous exposure on health and environmental issues associated with the contamination of firing ranges have come to light. The United States of America Environmental Protection Agency [4] has numerous reports concerning lead contamination on firing ranges and over 700 ranges have had to be cleaned by the US military alone [5]. Most of the lead contamination has resulted from the lead projectiles; however lead dust from small arms initiators and detonations also has a significant impact [6, 7].

The ideal solution would be a compound that has similar performance, is safer to handle, easier to synthesise and could replace the lead explosives. In this way only slight modifications would be required to the manufacturing process, thereby accelerating its implementation and ac-

ceptance. Some promising alternatives include nitro-tetrazole complexes [8], Bis-(5-nitro-2H tetrazolato-N2) Tetraamino Cobalt (III) Perchlorate (BNCP) and Mercuric-5-Nitrato Tetrazole (MNT) [9]. The mercury and cobalt compounds are also toxic and very sensitive so are not particularly suitable. The nitrotetrazoles are difficult to synthesize. There are a number of publications [10] which reviewed the more recent efforts.

Some promising materials are the long established complexes formed by metal cations with the nitrogen donor ligand, hydrazine [11]. A whole series of products for this ligand with ions of the first series transition metals with a number of oxidizing anions have been prepared [12]. The nickel salts Nickel Hydrazine Nitrate (NiHN),  $\text{Ni}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2$ , and corresponding perchlorate complex have shown promise. The perchlorate was extremely powerful explosive with estimated VoD of  $> 8000 \text{ ms}^{-1}$  but unfortunately it is highly sensitive even exploding during the preparation process [13] hence the absence of accurate performance data [14]. Research in China [15], India [16, 17] and at Cranfield University [18] have examined the nitrates explosive properties. There is some disagreement between centres on the sensitivity of NiHN. (See Table 1). Problem areas are impact sensitivity, (is the compound a primary, F of I 18, or secondary explosive, F of I 80) electrostatic spark sensitivity and

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**Table 1.** Comparison of properties for lead azide and NiHN.

Property	Lead Azide [31]	NiHN [15]	NiHN [30]
Velocity of Detonation ( $\text{m s}^{-1}$ )	4630	7000	7000
Impact (F of I (RDX = 80))	20	24	80
Figure of Friction N	0.1–	2–3	10
Electro-Static Discharge J	0.007	0.02	0.001
Temperature of Ignition $^{\circ}\text{C}$	327–360	167	219

temperature of ignition. Differences in the crystal morphology, such as particle size and crystal defects, of the solid produced could explain the discrepancy in sensitivity between authors even though both groups reportedly used the same preparation method. The first stage of this study examines the preparation conditions and stability properties of the title compound.

## 2 Experimental

All materials used both for the preparation and the analysis were supplied by Fisons of Loughborough, U.K. Nickel nitrate hexahydrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and hydrazine hydrate,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , 98% were reagent grades and used for the solid preparations. All chemicals used in the analysis procedures were of analytical grade, AR, or Chromatographic grade for the solvent used in the modified Andrews titration.

### 2.1 Preparation of NiHN

Three preparation methods were used in an attempt to control the solid crystallinity of the powder product. All methods were used on the 1 g scale initially as a safety precaution until the sensitivity had been evaluated before 10 g and larger preparations were attempted for a more detailed study. The first method was a modified literature method, and the other methods were developed in-house as part of the study.

### 2.2 Method 1

The literature preparation [12] was modified by adding hydrazine hydrate as a 20% solution rather than the 98% solution in the original method. This reduced the effective hydrazine concentration in the initial contact with the hot, 333 K, nickel nitrate solution (8%). The solution changed colour from pale green to pale purple within  $0.5 \text{ cm}^3$  of reagent added, with a purple solid being produced. The solid was separated by vacuum filtration, washed three times with ice cold water, three times with dry methanol and oven dried at 333 K. Yield was 1.05 g (90%). Following sensitivity trials the yield from the scale up was 99%.

### 2.3 Method 2

0.4 g of hydrazine mononitrate solid, previously prepared by potentiometric titration of hydrazine hydrate with nitric acid, was dissolved in  $10 \text{ cm}^3$  of a 10% nickel nitrate solution. The very limited quantity of cloudy material produced was separated off and then dilute ammonia, 0.5 M, was slowly added dropwise ( $>20$  minutes), with constant stirring. When the solution reached pH 7, addition of ammonia was stopped. Stirring was continued for a further 30 minutes before cooling in ice. The solid was filtered off and dried as described above. Yield 1.1 g (93%). Again when the scale was increased for batch production the yield increased to 98%.

### 2.4 Method 3

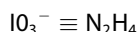
Nickel nitrate solution ( $50 \text{ cm}^3$  at 8%) was slowly added over 20 minutes to hot, 333 K, well stirred, 98% hydrazine hydrate. The initially clear solution started to turn a pale blue with the initial additions and the blue colouration deepened until  $\sim 15\%$  of the nickel solution was added when the purple precipitate started to appear. When the nickel solution addition was complete the mixture was digested for 10 minutes then cooled, the solid filtered off and treated as described above. After drying at  $60^{\circ}\text{C}$  o/n the yield was less than expected from the Nickel added. The filtrate still had a dark blue colour.

### 2.5 Analysis of Products

The dried products were analysed for nickel and hydrazine by the following methods.

The nickel contents of 0.1 M hydrochloric acid solutions, produced by acid digestion of weighed samples with hydrochloric acid, were determined by Atomic absorption spectroscopy using a Varian AA 10 spectrometer, calibrated with Nickel standard solutions, supplied by Fischer scientific Ltd. of Loughborough, Leicestershire U.K.

Hydrazine content was determined by titration with standard potassium iodate in the modified Andrews titration [19] using accurately weighed samples (0.1 g). The hydrazine content was calculated using the relationship



### 2.6 Spectroscopic Analysis

Infrared spectra of the 10 mm diameter pellets, 4% in dry "analar" potassium bromide, were recorded on a Bruker FTIR using Opus software for comparison with the literature data. The complementary Raman spectrum, which would

have indicated the nature of the symmetry within the structure, was unobtainable because the products from all preparations were ignited by the lowest power setting available on the Ocean Optics laser Raman spectrometer.

The low solubility of the solid in any of the non UV absorbing solvents prevented the recording of a conventional UV/Vis solution spectrum. The reflectance spectrum obtained from loose powder samples spread out on white card were recorded on a Perkin Elmer spectrometer. Preparation method 3 indicated the compound was soluble in concentrated Hydrazine Hydrate and the UV/Vis spectra were recorded on a series of solutions containing increasing quantities of NiHN.

None of the common, dry, NMR solvents dissolved sufficient quantity of the compound for a solution NMR to be obtained.

### 3 Results and Discussion

#### 3.1 Analysis

Analysis, Table 2, showed all three preparations produced the same compound.

**Table 2.** Analytical Results.

Preparation method	1	2	3	Theory
Nickel Content %	22.33	22.22	22.18	22.29
Hydrazine content %	33.89	33.91	34.15	33.98

Electron microscopy indicated differences in product particle sizes. Method 1 produced a larger particle size than the powders from method 2 and 3.

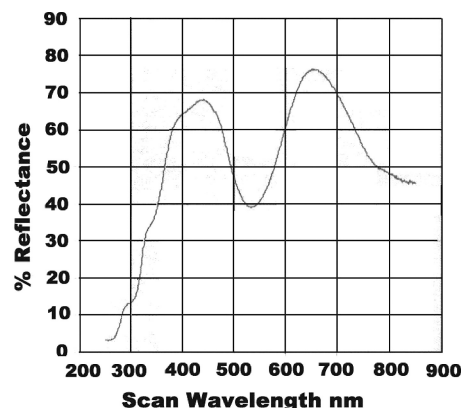
#### 3.2 Spectroscopy

The IR spectrum agreed with the literature confirming the identity of the product.

The UV reflectance spectrum of the powder, Figure 1, shows absorbance,  $\sim 560$  nm, due to nickel ions in an octahedral nitrogen field [20].

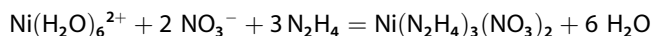
#### 3.3 Precipitation Process

Mixing hydrazine nitrate and nickel nitrate solutions produced a slight cloudiness but no precipitate. The concentration of free hydrazine in the solution is less than that required for precipitation. However if ammonia, a stronger base than hydrazine,  $pK_b$   $\text{NH}_3$  4.75,  $pK_{b1}$   $\text{N}_2\text{H}_4$  6.07, is introduced neutralization of the hydrazinium ion,  $\text{N}_2\text{H}_5^+$ , will generate free Hydrazine. In a titration experiment dilute am-

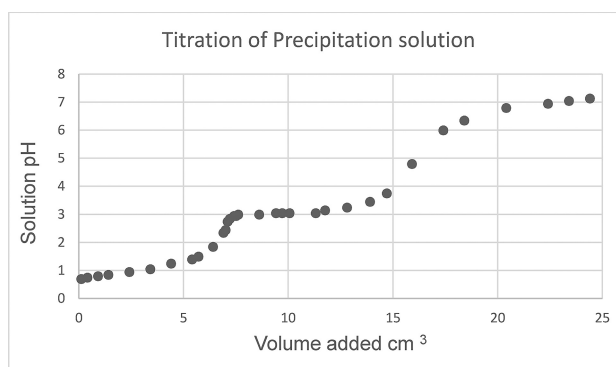


**Figure 1.** UV/Visible reflectance spectrum from NiHN powder.

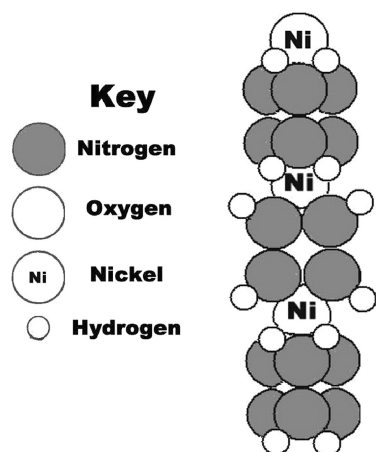
monia solution was added dropwise and the solution pH monitored, Figure 2. At pH 2.5, the ammonia drops of produced a trace of purple solid on the surface, but this re-dissolved with continued stirring. At pH  $\sim 3$  the precipitate was permanent and the pH remained at  $\sim 3$  until precipitation was complete when the pH started to increase. The stoichiometric equation for formation of the complex is



In the titration experiment and the normal preparation the first signs of a precipitate appear long before the ratio of free hydrazine to Nickel reaches the 3:1 given in the stoichiometric equation. The precipitation is driven by the very low solubility of the hydrazine complex. Reaction with three hydrazine molecules must be energetically favoured over any of the intermediate species. Amine compounds are better donors than water molecules [21]. The two nitrogen atoms in the hydrazine molecule are too close together, 0.147 nm, to occupy two adjacent positions in the Nickel coordination octahedron, minimum distance 0.197 nm, therefore these complexes must involve bidentate hydra-



**Figure 2.** Plot of precipitation solution pH as function of added ammonium hydroxide solution.



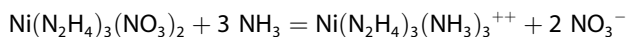
**Figure 3.** Projection perpendicular to axis of polymeric cation formed by hydrazines bridging nickel ions.

zine ligands bridging two nickel ions forming polymeric cations,  $(\text{Ni}(\text{N}_2\text{H}_4)_3^{2+})_n$ , Figure 3 [22] with a bonding energy contribution from the six membered ring formation [23]. Any suitable anion will then produce an insoluble precipitate [24] see section 3.4.

### 3.4 Solubility

NiHN was insoluble in any of the following common solvents DMSO, DCM, TCM methanol, ethanol, acetonitrile, benzene, benzonitrile, pyridine, N-methyl pyrrolidinone and dry acetone. Any traces of water catalyze the reaction of hydrazine with two molecules of ketone producing biso-propyl hydrazone thus dissolving the solid and generating nickel ion solution. Dilute acids  $>0.01$  M readily dissolved the pink material forming hydrazinium salts and a green solution of  $\text{Ni}^{2+}$  ions.

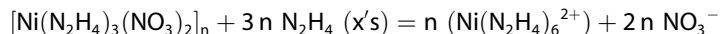
Addition of the powder to ammonia solution (2M) turns the liquid blue similar to that observed when Nickel nitrate is treated with excess of ammonia. An equilibrium is established between the tris hydrazine and an aminated species perhaps a triamine tri-hydrazine complex. Conversion of bridging hydrazines to mono coordinate hydrazines would produce soluble species



The free energy of formation favours the bidentate hydrazine over the monodentate hydrazine and ammonia hence the low solubility and the excess of ammonia required.

Preparation method 3 failed to produce a precipitate immediately or within a few  $\text{cm}^3$  added nickel solution indicating that the tris hydrazine complex may be soluble in hydrazine hydrate. Therefore weighed samples of the pink solid complex were added, under a nitrogen atmosphere, to

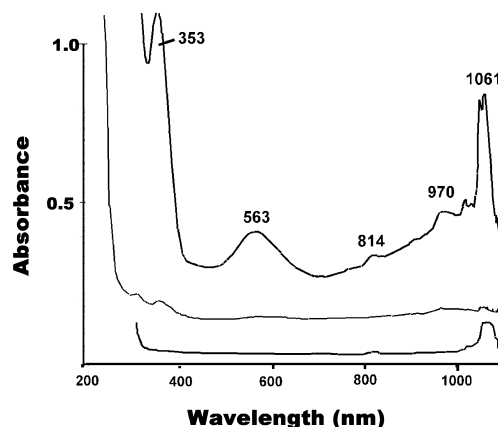
boiling hydrazine hydrate ( $40 \text{ cm}^3$ , 98%) until no further solid dissolved. After cooling to room temperature, residual solid was filtered off, washed dried and weighed and by difference the mass (2.511 g) of the NiHN in the solution was determined. Changes in UV visible spectra of this solution, as the solid increased, Figure 4, shows band, 563 nm, due to nickel in an octahedral nitrogen field [25]. A suggested reaction scheme is that the bidentate hydrazine polymeric cation is converted to a monodentate hydrazine octahedral nickel complex ion viz



The requirement for a tenfold excess of hydrazine hydrate indicates that the hexahydrazine complex is unstable with respect to the trishydrazine complex, which only dissolves when the above equilibrium is forced to the r.h.s, by excess of hydrazine hydrate. The insolubility of the trishydrazine complex is due to the polymeric cation formed by bridging hydrazines between Ni centres [26]. In the hexahydrazine complex discrete ions are present and hence it's solubility

#### 3.4.1 Conductivity Measurements

The increase in hydrazine hydrate solution conductivity observed when NiHN dissolves, see Table 3, is consistent with the formation of a soluble hexahydrazine nickel ion and nitrate ions. The major contributors to the conductivity are the hydronium and hydroxide ions produced by weak ionization of the hydrazine hydrate. These are more mobile than the bulky nickel hexahydrazinate ion hence the small increase in conductivity. The trihydrazinate is behaving as a



**Figure 4.** UV/Visible absorption spectrum of hydrazine hydrate solution containing increasing quantities of NiHN. Lowest trace is hydrazine hydrate solution. Middle trace first addition of NiHN powder. Upper trace 0.1 M NiHN in 98% hydrazine hydrate (1 mm path length).

**Table 3.** Conductivity of Hydrazine hydrate solutions with added NiHN.

Solution	Conductivity mS
Distilled water	0.03
95 % Hydrazine hydrate	15.03
" " + NiHN	15.42
5 % Hydrazine hydrate	1.53
" " + NiHN	1.64

weak electrolyte since it requires such a large excess of hydrazine to produce any significant solubility.

### 3.5 Equilibrium Formation Constants

An equilibrium constant for the formation of the trishydrazine complex precipitate is

$$K = [\text{Ni}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2] / [\text{Ni}(\text{H}_2\text{O})_6^{2+}] \cdot [\text{NO}_3^-]^2 \cdot [\text{N}_2\text{H}_4]^3$$

The measured solubility of NiHN is 3 mg in 100 cm<sup>3</sup> of water,  $1.06 \times 10^{-4} \text{ mol dm}^{-3}$ . A value of  $(4.79 \times 10^{-6} \text{ mol dm}^{-3})$  for the free hydrazine concentration in the solution at pH 3, was calculated from the equilibrium hydrolysis for a salt of a strong acid and weak base [27]. Using the initial concentrations of  $[\text{Ni}(\text{H}_2\text{O})_6^{2+}]$  ( $0.27 \text{ mol dm}^{-3}$ ),  $[\text{NO}_3^-]$ , ( $0.54 \text{ mol dm}^{-3}$ ) a value for the equilibrium constant can be calculated.

$$K = 1.06 \times 10^{-4} / 0.27 \times (0.54)^2 \times (4.79 \times 10^{-6})^3 \\ = 1.22 \times 10^{13} \text{ dm}^{15} \text{ mol}^{-5}$$

This value for the nitrate complex is greater than the equilibrium constant for the corresponding trishydrazine complexes formed in the presence of any other anion such as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$  or  $\text{BF}_4^-$ . See Table 4. Notice also that the solubility product, SP, which is simply the product of the concentrations, in  $\text{mol dm}^{-3}$ , of all the species of the complex present in solution, is also much lower for the nitrate complex than any other anion complex

**Table 4.** Comparison of Formation Constants,  $K_f$  for Nickel hydrazine compounds and their Solubility Products, S.P.

Compound	$\text{Ni}(\text{N}_2\text{H}_4)_3(\text{X}^-)_2$	
X	$K_f$	S.P.
$\text{NO}_3^-$	$3 \times 10^{14}$	$1.5 \times 10^{-22}$
$\text{SO}_4^{2-}$	$3.7 \times 10^{10}$	$7 \times 10^{-14}$
$(\text{Cl}^-)$	$(8 \times 10^8)$	$(5 \times 10^{-10})$
$\text{Cl}^-$	$8 \times 10^3$	$3.5 \times 10^{-11}$
$\text{BF}_4^-$	$\sim 10^7$	soluble

Footnote The bracketed Cl value is for the bishydrazine complex initially formed

### 3.6 Anion Dependency

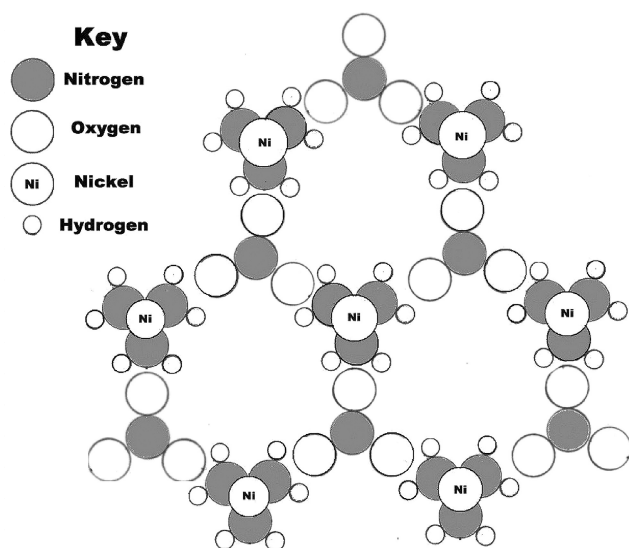
The borofluoride and iodide do not produce any precipitated complex and the solution contains a distribution of complexes with the number of incorporated hydrazine molecules ranging from 1 to 6 depending on the hydrazine concentration [24]. The sulphate shows similar properties to the nitrate. A solid trishydrazine complex is precipitated by the addition of small quantities of hydrazine but, unlike the nitrate, once all the nickel has been precipitated and further hydrazine solution is added the precipitate starts to re-dissolve with the formation of tetra-, penta- and hexa- hydrazinate complexes in solution [24]. The chloride is unusual with the initial precipitate is a bishydrazine complex,  $[\text{Ni}(\text{N}_2\text{H}_4)_2\text{Cl}_2]_n$ . The hydrazines form bridging links between the nickel ions in a planar polymeric chain and the chloride ions sit on the axial positions [25]. Further hydrazine molecules displace chloride from the nickel coordination sphere producing the tris hydrazine complex with the polymeric cation columns. Further addition of the hydrazine precipitation solution re-dissolves the trishydrazine precipitate forming hexahydrazine complexes as the end product.

These differences may be attributed to the hydrogen bonding of the anion groups to the coordinated hydrazine molecules. The iodide and tetrafluoroborate are not strong hydrogen bonders and hence will not hold the polymeric nickel hydrazine chains in a potential lattice formation. Chloride ion is not a particularly strong hydrogen bonding species and is taken into the nickel coordination sphere enabling bis hydrazine complexes, to be formed as the first stage. The sulphate exhibits hydrogen bonding with the coordinated hydrazines and hence forms a potential lattice configuration of the nickel hydrazine polymeric chains producing a precipitate however the tetrahedral configuration of the sulphate is not ideal for maximum bonding with the octahedral polymeric hydrazinate chains. This structure is easily destroyed, when further hydrazine is added, changing hydrazine coordination from a bidentate to monodentate ligand.

The nitrate anion is a strong hydrogen bonder and the trigonal planar structure is ideal for holding three polymeric nickel-hydrazine chains in an almost perfect hexagonal configuration structure, Figure 5. This structure will have a high lattice energy and high free energy of formation, resulting in the low solubility of the trishydrazine complex. No other nickel hydrazine nitrate complexes has been isolated probably because the trishydrazine polymer has a much higher stability than any other alternative. No precipitate solubility was observed following further addition of the hydrazine precipitation solution to the mixture. Limited solubility was only achieved by adding concentrated hydrazine solution (> 50 % hydrazine) to the separated solid precipitate.

It would be interesting to compare data for the chlorate  $\text{ClO}_3^-$  and perchlorate  $\text{ClO}_4^-$  both of which are potential hydrogen bonders for potential lattice formation but un-





**Figure 5.** NiHN crystal lattice looking down the polymer cation axis showing effect of nitrate hydrogen bonding on formation of hexagonal crystal structure.

fortunately they are both so initiation sensitive that there is no data available.

### 3.7 Hexahydrazine Complex

A value for the formation constant for the hexahydrazine complex can be determined from the solubility of the complex in hydrazine hydrate assuming the solubility of the trishydrazine complex is unchanged from that of pure water  $1.06 \times 10^{-4} \text{ mol dm}^{-3}$

$$K = \frac{[\text{Ni}(\text{N}_2\text{H}_4)_6^{2+}] \times [\text{NO}_3^-]^2}{[\text{Ni}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2] \times [\text{N}_2\text{H}_4]^3}$$

Quantity of NiHN soluble in hydrazine hydrate = 2.511 g in  $40 \text{ cm}^3 = 0.221 \text{ mol dm}^{-3}$   $[\text{N}_2\text{H}_4]$  in 98% hydrazine hydrate =  $19.6 \text{ mol dm}^{-3}$ . Substituting these values into the above equation gives a value for K for the formation of the hexahydrazine complex from trishydrazinate as  $0.056 \text{ dm}^3 \text{ mol}^{-1}$ . This result is consistent with the hexahydrazinate being metastable compared to the trishydrazine complex and is only formed under excess hydrazine conditions. Attempts to produce crystals of the hexahydrazinate nitrate complex by removal of excess hydrazine, under vacuum, produced a darker purple material than the prepared trishydrazinate but it analysed as pure trishydrazinate. Similar experiments with the chloride anion did not produce the hexahydrazinate complex but a product which analysed as between 4–5 hydrazines per nickel [25]. It is possible this product could be crystals with a hexahydrazinate core lattice surrounded by a trishydrazinate formed as the outer layer hydrazine is lost during purifica-

tion process. This would explain the solids variable composition. X-ray crystallography of the solid may elucidate the structure produced and clarify this aspect. Other authors [28] have suggested that the hexahydrazinate can be produced by high vacuum, low temperature (270 K) crystallization from solutions of anhydrous nickel chloride in absolute anhydrous hydrazine systems. This behaviour of the nickel complex is in contrast to the corresponding cobalt complex where the hexahydrazine complex can be isolated from water containing solutions [29]. Further work is required to produce pure trishydrazinate complexes with different, measured, particle size distributions and test their sensitivity to various stimuli to eliminate the dichotomy in the literature values by different authors. Also investigation of the solid produced when anhydrous nickel nitrate is added to anhydrous hydrazine under nitrogen might further clarify the nitrates unique properties.

## 4 Conclusions

The conditions for the precipitation of the title compound under three different procedures and its solubility in a range of solvents have been determined. Values for the equilibrium constants governing the title compounds formation and solubility in excess hydrazine forming a postulated hexahydrazinate complex have been determined. A comparison with other nickel hydrazine complexes with other anions has shown that the nitrate produces the least soluble trishydrazinate complex. Strong hydrogen bonding between the nitrate anion and the coordinated hydrazine molecules producing a complete three dimensional polymeric crystalline species was suggested as the origin of the low solubility of the trishydrazinate complex and the failure to form a crystalline hexahydrazinate species. Hexahydrazinate ions were only formed in concentrated hydrazine hydrate solution.

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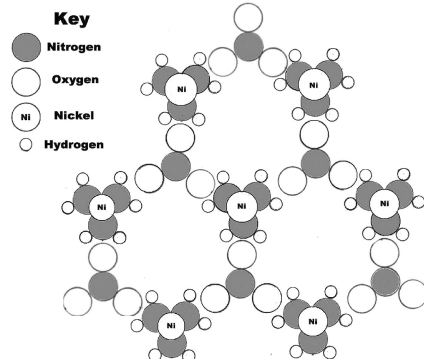
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**Investigation of Preparation, Solubility and Stability Properties of Nickel Hydrazine Nitrate (NiHN)**

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