inger and Burg[7] for the diammoniate contains six B–H bonds which, judging from the spectra of analogous molecules such as propane and dimethyl ether, would be expected to give a very complicated spectrum in the B–H stretching region. That such a pattern fortuitously would match that obtained by superimposing two additional frequencies on the borohydride spectrum seems extremely unlikely, and to this extent the spectral evidence does not agree with their proposed structure.

Decomposition Product of Ammonium Borohydride.—Chemical evidence has been given elsewhere[9] to the effect that if liquid ammonia solutions of NH_4BH_4 are evaporated to dryness and the solid allowed to warm to room temperature, the solid evolves hydrogen and leaves a product which has the properties of the diammoniate of diborane. The spectrum of this decomposition product prepared as described was obtained in the present work largely to supply confirmatory evidence. Due to experimental difficulties, the solutions obtained were more dilute than those of the diammoniate and were not as "clean" optically. However, the frequency values in Table II match those of the diammoniate within experimental error and the band outline in the B–H stretching region also agreed very closely. The identity of the decomposition product with the diammoniate thus appears confirmed.

Product of the Diammoniate–Ammonium Bromide Reaction.—As a consequence of the instability of solid ammonium borohydride at room temperature, treatment of the diammoniate with ammonium bromide under the proper conditions can result in the destruction of the borohydride ion present and its replacement by the bromide ion. In terms of the structure proposed previously,[5] the reaction can be written

$$[H_2B(NH_3)_2^+](BH_4^-) + 2NH_4Br \longrightarrow 2[H_2B(NH_3)_2^+](Br^-) + 2H_2$$

Details of this reaction also have been given elsewhere[5] and the properties of the product described. The Raman frequencies observed for this reaction product dissolved in liquid ammonia are given in Table II. Inspection shows that all values listed also appear in the diammoniate spectrum and, further, that the frequencies of the borohydride ion plus those of the NH_4Br reaction product together account for all bands observed in the diammoniate spectrum. The spectral evidence thus is strong that the reaction written above is correct. Two bands appear to be common to the spectrum of the cation and to the borohydride ion, namely, the bands at about 1210 cm.$^{-1}$ and their overtones at about 2405 cm.$^{-1}$. Apparently the bending frequency of the BH_2 group in the cation occurs at almost the identically same position as ν_2 of the borohydride ion. Due to the small, and in this case unknown, effect of the cation on the borohydride frequencies plus the inherent experimental uncertainty in measuring the positions of weak and rather broad bands, the two cannot clearly be distinguished.

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Ann Arbor, Mich.

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[9] R. W. Parry, D. R. Shultz and P. R. Girardot, This Journal, **80**, 1 (1958).

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Reaction of Tetrasulfurtetranitride with Nickel Chloride

By T. S. Piper

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The reaction of nickel chloride with tetrasulfurtetranitride in alcohol solution, which has been reported to yield NiS_4N_4, has been reinvestigated and found to produce the series of compounds $NiS_4N_4H_2$, NiS_5N_3H and NiS_6N_2.

M. Goehring and her co-workers have discovered an interesting series of compounds of transition metals to which was ascribed the type formula $M(NS)_4$; compounds were reported for Ni,[1,2] Co,[2,3] Fe,[2,4] Pd[2,5] and Pt.[5] Preliminary studies of the platinum compound by X-ray diffraction[6] have shown the presence of two –N–S–N–S– bidentate ligands in a planar *cis* configuration. With a view to obtaining further structural information an investigation of the chemistry and spectra of the nickel compound has been undertaken.

Experimental[7]

The Preparation of $NiS_4N_4H_2$.—The reported procedure[2] combining S_4N_4 and anhydrous $NiCl_2$ in refluxing alcohol was used. Twenty grams of S_4N_4 and 25 g. of anhydrous $NiCl_2$ were mixed with 700 ml. of anhydrous methyl alcohol and heated to reflux under nitrogen for eight hours. The alcohol was then distilled out of the reaction flask at reduced pressures and the solid which remained behind was extracted with one liter of benzene. The benzene solution was run through a chromatographic column (55 mm. diameter) containing four pounds of acid washed alumina (Merck and Co., Inc.). A red fraction was eluted with the benzene leaving a purple band on the column. The solid

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[1] M. Goehring and A. Debo, *Z. anorg. allgem. Chem.*, **273**, 319 (1953).

[2] M. Goehring, K.-W. Daum and J. Weiss, *Z. Naturforsch.*, **10b**, 298 (1955).

[3] K.-W. Daum, M. Goehring and J. Weiss, *Z. anorg. allgem. Chem.*, **278**, 260 (1955).

[4] M. Goehring and K.-W. Daum, *ibid.*, **282**, 83 (1955).

[5] E. Fluck, M. Goehring and J. Weiss, *ibid.*, **287**, 51 (1956).

[6] J. Weiss, *Angew. Chem.*, **69**, 108 (1957).

[7] I am indebted to Mr. J. Nemeth, Miss C. Higham and Mrs. M. Stingl for the carbon, hydrogen and nitrogen analyses and also to Mr. James Brader who kindly measured the infrared spectra.

remaining in the reaction flask was extracted with three one-liter portions of acetone and put on the column. The purple band was eluted slowly by acetone and completely by a solution of one volume of ethanol to four volumes of acetone. Since a clean separation of the two colored fractions was not achieved in the first chromatogram, the above procedure was repeated twice on the black solid obtained by evaporation of the second fraction. The crude black crystalline solid completely free of the first fraction weighed 11.6 g. Some of it was further purified by repeated chromatography, crystallization from acetone by slow addition of pentane and finally sublimation *in vacuo* at 140° and 0.002 mm. This purified material melted at 154.7–155.0° with decomposition (reported[1] for NiN_4S_4, 153°).

Anal. Calcd. for $NiS_4N_4H_2$: Ni, 23.95; S, 52.1; N, 22.67; H, 0.82 (Calcd. for NiS_4N_4: Ni, 24.15; S, 52.8; N, 23.05). Found: Ni, 23.85; S, 52.0; N, 22.89; C, 0.37, 0.24, 0.29; H, 0.84, 0.80, 0.78.

The three sets of carbon and hydrogen microanalyses were run on different samples; large samples (about 20 mg.) were used to ensure an accuracy of ±0.04% absolute. The small amount of carbon present may be due to solvent but it is more likely a determinate error since it was found even for the sublimed samples. In any case it is so small that only about 0.04% hydrogen may be ascribed to hydrocarbon impurities. The hydrogen must be obtained by reaction with the solvent; indeed no product was formed when the alcohol solvent was replaced by carbon disulfide or benzene.

The Separation of NiS_5N_3H.—A black solid mixed with sulfur was obtained by evaporation of the first chromatographic fraction. The solid was extracted with 40 ml. of hot benzene; the solution was cooled and diluted with 200 ml. of pentane. The solution was then filtered and passed through 200 g. of acid washed alumina in a column whose diameter was 20 mm. A green fraction advanced with the solvent front while the red fraction advanced but slowly. Extraction of the solid was repeated until all of the solid was on the column. The concentration of benzene in the eluting solvent was increased slowly; the red fraction was eluted between 50% benzene in pentane and pure benzene. The black solid obtained by evaporating the red fraction was purified of the substances in the green fraction by dissolving it in a minimum amount of benzene and crystallizing it out by slow addition of pentane. There was obtained 0.625 g. of fairly pure black crystals. Further purification was effected by repeated crystallization from mixtures of benzene and pentane, also crystallization from methanol to remove traces of $NiS_4N_4H_2$, and finally by sublimation *in vacuo* at 100° and 0.002 mm. It melted at 135.5–136.0° with decomposition.

Anal. Calcd. for NiS_5N_3H: Ni, 22.3; S, 61.2; N, 16.03; H, 0.38. Found: Ni, 22.33; S, 60.5; N, 16.21; C, 0.20; H, 0.41.

The Separation of NiS_6N_2.—Purification of the substance responsible for the green color was difficult due to the presence of sulfur. It was dissolved in pentane and passed through two pounds of acid-washed alumina. The sulfur preceded the green fraction slightly; both were eluted with pentane. This was repeated twice and 9 mg. of black needle-like crystals was obtained. It was crystallized from methanol and sublimed at 60° and 0.002 mm.; it melted at 118.1–118.5°.

Anal. Calcd. for NiS_6N_2: Ni, 21.0; S, 69.0; N, 10.0. Found: Ni, 21.0; S, 68.1; N, 9.93.

All three compounds form black crystals; $NiS_4N_4H_2$ occurs as feathery needles, NiS_6N_2 as needles. $NiS_4N_4H_2$ is insoluble in pentane, slightly soluble in benzene giving dichroic solutions (green to reflected light, permanganate colored to transmitted light) and soluble in acetone and alcohol giving permanganate colored solutions. NiS_5N_3H is considerably more soluble in benzene and gives red solutions. NiS_6N_2 is somewhat soluble in pentane, quite soluble in benzene and carbon disulfide but not as soluble in oxygenated solvents. Solutions of these compounds in benzene are not affected by shaking with water at first, but on standing slow decomposition occurs. Decomposition with acid is faster. With dilute bases $NiS_4N_4H_2$ and NiS_5N_3H but not NiS_6N_2 are extracted into the water phase with little change in color. Upon neutralization, they may be extracted back into the benzene.

Samples were titrated[8] with sodium hydroxide in solutions made from two volumes of ethanol to one of water. For $NiS_4N_4H_2$ the first ionization constant, pK_1, was found to be 10.9. In this system pK_2 could not be measured but since a well-defined break occurred in the titration curve after addition of one equivalent of base per mole of nickel it must be greater than 13. For NiS_5N_3H the pK was found to be 9.2. An attempted titration of $S_4N_4H_4$ showed that the first ionization constant is greater than 12 or 13; it is not soluble in 1 M sodium hydroxide solution.

Several attempts were made to form derivatives by replacing this active hydrogen. Decomposition occurred when $NiS_4N_4H_2$ was treated with methyl iodide or p-toluenesulfonyl chloride in the presence of various bases. With diazomethane extensive decomposition occurred but it was possible to isolate by chromatography a mixture of the monomethyl and dimethyl derivatives as evidenced by nitrogen, carbon and hydrogen analyses, and infrared spectrum. However, the yield was less than 1% so this reaction was not pursued further.

When pure NiS_5N_3H was chromatogramed on acid-washed alumina a small part of it was converted to approximately equal amounts of NiS_6N_2 and $NiS_4N_4H_2$; but if the alumina was used a second time this reaction did not take place. By using a sufficiently large amount of alumina NiS_5N_3H may be converted in good yield to NiS_6N_2. Heat also brings about this transformation. In one experiment 40 mg. of NiS_5N_3H was held at 90° in a sealed tube with 1 ml. of benzene for three days. Chromatography on 7 g. of acid-washed alumina yielded 7 mg. of NiS_6N_2, 3 mg. of $NiS_4N_4H_2$ and 15 mg. of starting material. An attempted reaction of $NiS_4N_4H_2$ with sulfur in organic solvents yielded no NiS_5N_3H or NiS_6N_2.

Infrared Spectra.—The infrared spectra recorded in the following table were measured using a Perkin–Elmer Spectrophotometer Model 21 with a sodium chloride prism. The deuterium derivatives were prepared by dissolving the compound in tetrahydrofuran, adding a thousand-fold excess of deuterium oxide and then pumping off the solvent. The starting compound was regenerated by treating the deuterium derivative with water in this fashion. Complete exchange had occurred within 20 minutes, the time required to pump off all the solvent. All results in Table I are expressed in cm.$^{-1}$. The spectra were obtained from Nujol mulls and pressed potassium bromide discs.

TABLE I

INFRARED SPECTRA[a]

$NiS_4N_4H_2$	$NiS_4N_4D_2$	NiS_5N_3H	NiS_5N_3D	NiS_6N_2
3235m	2435m	3110m,b	2360m,b	984s
3095m,b	2360m,b	1220mw,b	1270w	720vs
2460vw	1040vs	1040ms	1107w,b	707vs
2300vw	985v,b	968s	1040s	
1243w,b	952vw	890ms	968s	
1167s	840w	710vs,b	885w	
1040vs	827m		820mw,b	
892s	707vs,b		760w	
705vs,b	692sh		710vs,b	

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; b, broad; sh, shoulder.

Nuclear Magnetic Resonance Spectra.—The nuclear spin resonance spectra of the hydrogen atoms were obtained for $NiS_4N_4H_2$ and $S_4N_4H_4$. Low solubility prevented observation of the spectrum of NiS_5N_3H. A Varian High Resolution Spectrometer was used. Samples were dissolved in tetrahydrofuran and a sealed capillary tube filled with water was inserted for reference. The chemical shift in p.p.m. of the applied field at which resonance for the reference substance was observed was found to be −4.6 p.p.m. for $NiS_4N_4H_2$ and −1.3 p.p.m. for $S_4N_4H_4$.

Visible and Ultraviolet Spectra.—The main peaks in the spectra are presented in Table II. The definition of the ex-

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[8] The concentration of nickel compound was about 3 millimolar. No correction for ionic strength was made at this low concentration. A rough comparison between results in water and 67% ethanol may be made obtained by reference to results obtained by K. L. Rinehart, Jr., K. L. Motz and S. Moon, THIS JOURNAL, **79**, 2752 (1957). For example, in the case of benzoic acid pK was found to be 4.2 in water and 7.4 in 67% ethanol.

tinction coefficient adopted here is the negative logarithm to the base ten of the fraction of light transmitted by a one molar solution one cm. in length.

TABLE II

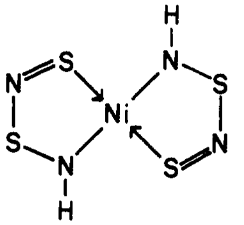
VISIBLE AND ULTRAVIOLET SPECTRA

Compound	Solvent	Wave length, Å.	Molar extinction coefficient, M^{-1} cm.$^{-1}$
$NiS_4N_4H_2$	Ethanol	5630	1,770
		4045	3,630
		~3100 sh	12,000
		2770	17,800
NiS_5N_3H	Ethanol	5400	1,270
		4670	1,800
		3020	17,500
NiS_6N_2	Cyclohexane	7200	800
		6510	2,100
		4250 sh	2,300
		3200	18,000

Discussion

The cumulative evidence from analyses, spectra and chemical reactions leaves no doubt about the correctness of the assigned molecular formulas. That $NiS_4N_4H_2$ and NiS_6N_2 may be obtained from NiS_5N_3H under mild reaction conditions is excellent evidence that these compounds form a structurally related series in which the bidentate ligands S_2N_2H and S_3N are present; the S_3N ligand may be thought of as derived from the S_2N_2H ligand by replacement of the NH group by a sulfur atom. To emphasize the structures involved the formulas may be written as $Ni(S_2N_2H)_2$, $Ni(S_2N_2H)(S_3N)$ and $Ni(S_3N)_2$.

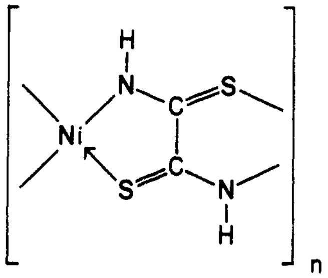
For $NiS_4N_4H_2$ it is not known which *cis–trans* isomer and which tautomer occurs. For the purpose of illustration one of the more likely structures is given.



Similarly the S_3N ligand may have the form –S–N–S–S– or –N–S–S–S–. To decide this question X-ray diffraction studies have been begun at this Laboratory by Dr. T. L. Brown.

That the hydrogen is attached to nitrogen is shown by the infrared spectra. The bands at about 3000 cm.$^{-1}$ are readily assigned to N–H stretching vibrations; this is confirmed by the shift to about 2400 cm.$^{-1}$ upon exchange with D_2O. Lack of pronounced shift upon deuteration identifies the absorption bands due to skeletal motions. All the compounds show such bands in the region 700–720 cm.$^{-1}$. Another strong band due to skeletal motions occurs at about 1000 cm.$^{-1}$: at 1040 cm.$^{-1}$ for the S_2N_2H ligand; at 968 cm.$^{-1}$ for the S_3N ligand in NiS_5N_3H; and at 984 cm.$^{-1}$ for the S_3N ligand in NiS_6N_2; the high frequency of this second band suggests multiple bonds between nitrogen and sulfur. The essential similarity of these bands for all the compounds is good evidence of similar skeletal structures of all the compounds at least as far as the nitrogen atoms are concerned, since their motions contribute most to these higher lying frequencies.

The N–H groups in these compounds are considerably stronger acids than such groups in organic compounds or even in $S_4N_4H_4$; there must be considerable delocalization of the negative charge in the anion by formation of multiple bonds. The enhanced acidity of such groups in metal compounds is common. In this respect as well as several others, these compounds call to mind the nickel salt of dithioöxamide, a black polymeric material which dissolves in bases; the infrared spectrum showed that the hydrogen is attached to nitrogen. Thus the acidity of these N–H groups is weak evidence that in $NiS_4N_4H_2$ and NiS_5N_3H they are adjacent to the metal, a point which is being further investigated. It may be noted for the N–H group in these compounds as compared to such groups in typical organic compounds that as usual the trend toward increased acidity is paralleled by a trend to decreased chemical shift.



URBANA, ILLINOIS