Reaction between S_4N_4 and Ni^{2+} in Dimethyl Sulphoxide. Formation and Characterization in Solution of $S_4N_2(NH_2)_2$, a Novel Sulphur–Nitrogen Heterocycle Precursor of $[Ni(S_2N_2H)_2]$

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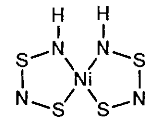
The complex $[Ni(S_2N_2H)_2]$ undergoes a protonation reaction in dimethyl sulphoxide (dmso) solution upon addition of stoichiometric amounts of a strong acid, giving $[Ni(S_2N_2H_2)(S_2N_2H)]^+$. The value of the proton association constant has been determined potentiometrically, $\log K_1 = 3.3$. Proton and ^{15}N NMR studies reveal that the proton binds at one NH group, resulting in the formation of the bidentate co-ordinated ligand $S{=}N{-}S{-}NH_2$. This metal complex is also formed very slowly at room temperature, in the reaction of S_4N_4 and Ni^{2+} in dmso. The reaction rate increases dramatically on addition of stoichiometric amounts of sodium acetate or NBu_4OH. The compound S_4N_4 does not react directly with the metal ion but with the trace amounts of water contained in the solvent, resulting in the formation of $S_4N_2(NH_2)_2$ which then reacts with Ni^{2+} ions to give the final metal complex. The novel sulphur–nitrogen heterocycle $S_4N_2(NH_2)_2$ has been characterized in solution by molecular exclusion chromatography, ion exchange, UV/VIS, IR and NMR (^1H and ^{15}N) spectrophotometry. Comparison of the NMR spectra with those of the nickel(II) complex suggests that $S_4N_2(NH_2)_2$ consists of a non-planar S_4N_2 ring with two exocyclic NH_2 groups bonded to opposite sulphur atoms in the ring and on the same face. On the basis of this structure the formation of $[Ni(S_2N_2H)_2]$ is easily understood.

Sulphur and nitrogen may combine into a large variety of compounds. Most sulphur–nitrogen species are cyclic and can be neutral molecules (*e.g.* S_4N_4, S_2N_2), cations (*e.g.* $S_4N_3^+$, $S_5N_5^+$) or anions (*e.g.* $S_3N_3^-$, $S_4N_5^-$). Although some have been known for many years, our understanding of this field is still only partial. It is very difficult and often impossible to predict the structures and reactivity of S–N compounds. The S–N chemistry has grown dramatically in the last twenty years and has been reviewed many times.[1–13]

Many S–N species can serve as ligands in metal complexes. Indeed, some open-chain S–N anions (*e.g.* $S_2N_2H^-$, $S_2N_2^{2-}$) are only stabilized by co-ordination to a metal ion and are non-existent in free form. The $S_2N_2H^-$ ion has been characterized as a transient species in liquid ammonia.[14] Metal complexes with S–N ligands have been recently reviewed too.[15,16] The compounds $[M(S_2N_2H)_2]$ (M = Ni, Pd, Pt or Co) are the most frequently studied and best characterized of these, particularly the nickel(II) compound.

The complex $[Ni(S_2N_2H)_2]$ is obtained in high yield from the reaction of anhydrous $NiCl_2$ with tetrasulphur tetranitride, S_4N_4, in refluxing methanol.[17] It has been shown through X-ray studies[18,19] to contain bidentate ligands $S_2N_2H^-$ ($S{=}N{-}S{-}NH^-$) which form five-membered chelate rings with the metal ion. The geometry around the nickel(II) is square planar with the NH groups in a *cis* arrangement **1**.



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The complex $[Ni(S_2N_2H)_2]$ undergoes a variety of reactions that are largely dependent on the reactivity of the NH protons. It is deprotonated in a basic medium giving the anionic complexes $[Ni(S_2N_2H)(S_2N_2)]^-$ and $[Ni(S_2N_2)_2]^{2-}$.[20,21] The hydrogen atoms are easily substituted by organic groups; more than thirty mono- and di-substituted derivatives have been reported and in some cases structurally characterized.[22,23] Reaction with CN^- results in the substitution of a $S_2N_2H^-$ ligand to form $[Ni(CN)_2(S_2N_2H)]^-$.[24] The complex $[Ni(S_2N_2H)_2]$ is also a useful precursor in the synthesis of other S–N compounds. Reaction with S_2Cl_2 gives S_4N_2 whereas with $COCl_2$ and $SOCl_2$ the five-membered cyclic molecules S_2N_2CO and S_3N_2O are formed, respectively.[25]

Although the structure and reactivity of $[Ni(S_2N_2H)_2]$ are well established, it is surprising that nothing is known about the nature of the formation reaction in solution. Obviously, it is not simple since beginning from an S_4N_4 cluster two $S_2N_2H^-$ ligands are obtained. Therefore during the reaction the fragmentation, reduction and protonation of the S_4N_4 molecule must arise though not necessarily in this order. However, the only indication found in the literature is that during the reaction 'abstraction' of protons from the solvent must take place,[20] which clearly does not contribute much to the understanding of its nature.

In this paper we report a study of the formation reaction of $[Ni(S_2N_2H)_2]$ in solution. We have observed that this complex is slowly formed at room temperature in the reaction of Ni^{2+} and S_4N_4 using dimethyl sulphoxide (dmso) as solvent. This has enabled its study through physical techniques such as UV/VIS spectrophotometry and ^1H and ^{15}N NMR spectroscopy. As a result we have been able to establish a detailed picture of how the reaction takes place, identifying and characterizing the intermediate species which are formed. For comparative reasons we have also studied the behaviour in dmso of the nickel complex $[Ni(S_2N_2H)_2]$ which led us to find new aspects of its reactivity.

Experimental

Materials.—The compounds S_4N_4,[26,27] $NiCl_2$[28] and $[Ni(S_2N_2H)_2]$[17] were all synthesised and purified according to literature methods. All reactions and the manipulation of moisture-sensitive reagents were carried out under an atmosphere of dinitrogen. **CAUTION**: S_4N_4 may explode if subjected to heat or friction. The recommended precautions for handling S_4N_4 should be followed.[29]

The compound $S_4{}^{15}N_4$ was prepared from $^{15}NH_4Cl$ by adapting the procedure reported in the literature.[30] We also synthesised $[Ni(S_2{}^{15}N_2H)_2]$ from this isotopically enriched tetrasulphur tetranitride. The compound $^{15}NH_4Cl$ (99% ^{15}N) was supplied by MSD Isotopes. All the other chemicals were reagent-grade commercial samples used as received.

Solution studies were carried out in dmso as solvent. The reliability of the spectrophotometric measurements depended upon the purity of dmso, more precisely upon the water content. Before use, it was run through an alumina column (diameter 25 mm), followed by double distillation under reduced pressure [*ca.* 2 Torr (*ca.* 266 Pa)] and finally kept in the dark over 4 Å molecular sieves. This 'dry' dmso retains some water as shown by the ^1H NMR spectrum. All the other solvents were dried and freshly distilled before use. Benzene (4 Å), acetonitrile (CaH_2, 3 Å), methylene dichloride ($CaCl_2$, 4 Å), carbon tetrachloride (P_2O_5, 4 Å), methanol (CaO, 3 Å) and $(CD_3)_2SO$ (99.5%) (4 Å).

Sephadex G-10 was used in the molecular exclusion chromatography experiments and Amberlite IRA-400 (Cl) standard grade resin in the ion-exchange experiment.

Physical Techniques.—Absorption spectra in the UV and visible regions were recorded on a Philips Analytical SP8-100 spectrophotometer using 1 cm and 0.1 cm quartz cuvettes thermostatted at 25.0 ± 0.1 °C, infrared spectra as KBr pellets or Nujol mulls by using a Perkin-Elmer 1750 FTIR spectrophotometer. The spectra of species in solution were recorded by disposing a thin layer of liquid between two AgCl discs.

Proton NMR spectra were recorded at 200 MHz on a Brüker AC-200 spectrometer, operating in the Fourier-transform mode. Useful spectra could usually be obtained at 25 °C, with 150–300 scans and spectral width 3–8 KHz. Solutions of varying (8.5×10^{-2}–1×10^{-2} dm^{-3}) concentrations in $(CD_3)_2SO$ as solvent were used. As an external reference, $SiMe_4$ in the same solvent placed in a tube coaxial to the one containing the sample solution was used.

Nitrogen-15 NMR spectra were recorded on a Varian-XL 300 spectrometer operating at 30.41 MHz at 20 and 55 °C. Solutions (10^{-2} mol dm^{-3}) of ^{15}N-enriched samples (99% ^{15}N) in dmso [containing 10% $(CD_3)_2SO$ to provide the locking signal] were used. Samples were contained in 10 mm outside diameter tubes and the chemical shifts were measured with respect to an external sample of $CH_3{}^{15}NO_2$ contained in a 2 mm capillary held concentrically in the sample tube. Useful spectra could usually be obtained with 150–2300 scans, a pulse of 10–20 μs, a relaxation delay of 2–30 s and a spectral width of 21.367 KHz. In some cases ^{15}N NMR spectra were recorded under similar conditions on a Brüker AC-200 spectrometer operating at 20.282 MHz.

Electromotive force measurements in dmso solution were performed with a Radiometer 84 pH-meter, using a GK 2401 C combined glass electrode in which the saturated aqueous KCl solution of the reference electrode was replaced by a saturated methanolic KCl solution. The electrode was immersed in dmso solution for several days before use. Its response was not instantaneous, but reliable potential measurements were obtained after 5–10 min. Measurements were carried out at 25.0 ± 0.1 °C in a nitrogen atmosphere and 0.1 mol dm^{-3} $KClO_4$. Nernst's equation $E = E^{\circ\prime} + 0.059 \log [H^+]$ was strictly obeyed under the conditions mentioned above, at least over the hydrogen-ion concentration range between 10^{-2} and 5×10^{-7} mol dm^{-3}. The $E^{\circ\prime}$ value was determined by titrating a toluene-4-sulphonic acid solution with tetrabutylammonium hydroxide.

The column used in molecular exclusion chromatography was 30 cm × 2 cm internal diameter with a bed height of 20 cm. The bed volume was 2–3 cm^3 per g of dry Sephadex. During swelling (*ca.* 3 h) under an argon atmosphere the mixture Sephadex–dmso was stirred carefully to avoid breaking the beads. Experiments with ion-exchange resins were carried out using *ca.* 0.4 g of resin in 5 cm^3 of the sample solution in a closed container.

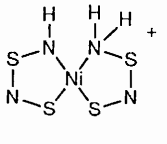
Results and Discussion

Solutions of $[Ni(S_2N_2H)_2]$ *in dmso.—Protonation equilibrium.* The complex $[Ni(S_2N_2H)_2]$ is soluble in dmso giving a violet solution which displays three absorption bands in the UV/VIS spectrum at 280 ($\varepsilon = 1.2 \times 10^4$) (shoulder at 300) 400 ($\varepsilon = 2.7 \times 10^3$) and 550 nm ($\varepsilon = 1.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}). This spectrum agrees well with that reported in other solvents.[31] Solutions of $[Ni(S_2N_2H)_2]$ in dmso are not indefinitely stable, decomposing very slowly. So, the absorbance at 400 nm of a 10^{-3} mol dm^{-3} solution decreases by about 10% after 1 week. Addition of an excess of potassium hydrogenphthalate stabilizes the solution which remains practically unaltered during this time. Stoichiometric amounts of toluene-4-sulphonic acid stabilize the solution too, but an excess of acid increases the decomposition rate.

The ^1H NMR spectrum shows only one signal at δ 10.8 and the ^{15}N NMR spectrum two signals at δ −39 and −144. Both results are consistent with the presence of two equivalent hydrogen atoms and four nitrogen atoms in two non-equivalent sets in the $[Ni(S_2N_2H)_2]$ molecule. No splitting of signals was observed in the proton-coupled ^{15}N NMR spectrum but we can assign the signal at δ −39 to the N=S groups and that at δ −144 to the NH groups on the basis of published ^{15}N chemical shift values.[32–34]

Addition of stoichiometric amounts of a strong acid to a $[Ni(S_2N_2H)_2]$ solution leaves the optical spectrum unaltered but modifies significantly both ^1H and ^{15}N NMR spectra. The ^1H NMR spectrum shows, besides the initial signal, which under these conditions appears a little displaced at δ 11, a new signal at δ 7.1 resolved into a triplet with *J*(NH) 51 Hz, resulting from proton coupling to nitrogen. The appearance of this signal is not instantaneous, its intensity increasing slowly with time. The ^{15}N NMR spectrum of an acidified solution of $[Ni(S_2{}^{15}N_2H)_2]$ shows, besides the characteristic features of the original metal complex, a new strong signal at δ −352. In the proton-coupled spectrum (Fig. 1) the signal at δ −144 is resolved into a doublet with *J*(NH) 76 Hz, supporting unambiguously its assignment to NH groups, and the new signal at δ −352 appears as a triplet with *J*(NH) 71 Hz, revealing the formation of NH_2 groups.

These results indicate that $[Ni(S_2N_2H)_2]$ undergoes a protonation reaction resulting in the formation of the cationic complex $[Ni(S_2N_2H_2)(S_2N_2H)]^+$ **2**. The proton binds the NH group of one ligand to give the bidentate co-ordinated ligand S=N–S–NH_2. The NH_2 group is responsible for the signals at δ 7.1 and −352 in the ^1H and ^{15}N NMR spectra, respectively.



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We have also studied this protonation reaction by potentiometry. As the protonation equilibrium of the metal complex is slow, the proton association constant was determined using a discontinuous procedure. To that end we prepared a series of solutions whose metal complex concentration was kept constant and the molar ratio acid/complex was varied from 0 to 1 : 1. The solutions were left until equilibrium was reached, and the proton concentration was measured after some days. The degree of protonation, $\bar{j}$, was obtained from the potentiometric

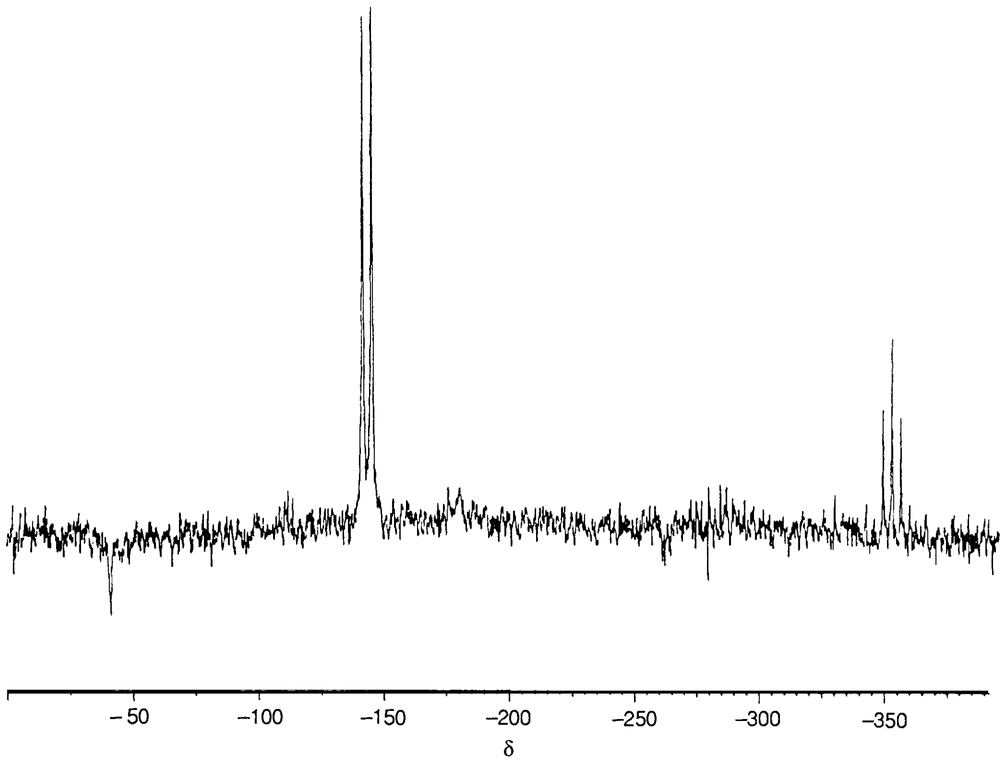


Fig. 1 Proton-coupled ^{15}N NMR spectrum of a 2.5 × 10^{-2} mol dm^{-3} [$Ni(S_2{}^{15}N_2H)_2$] solution after addition of hydrochloric acid (2.5 × 10^{-2} mol dm^{-3})

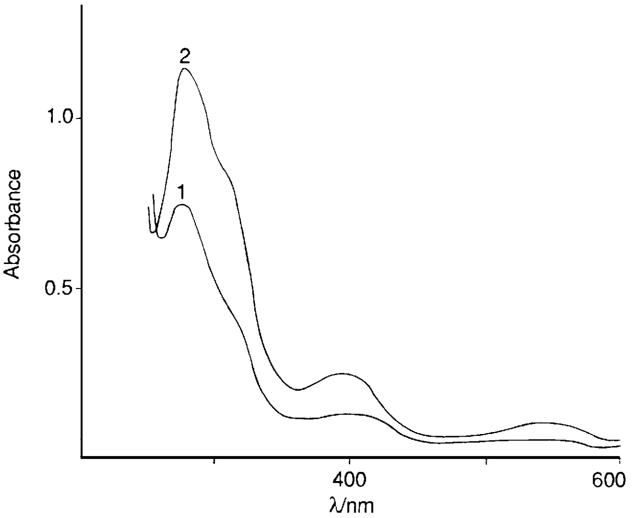


Fig. 2 UV/visible spectrum of (1) a solution of S_4N_4 (10^{-3} mol dm^{-3}) and Ni^{2+} (10^{-2} mol dm^{-3}) 14 d after preparation; (2) 10^{-3} mol dm^{-3} [$Ni(S_2N_2H)_2$]; (l = 0.1 cm)

data. A plot of $\bar{j}/1 - \bar{j}$ *versus* [H^+] gave a straight line whose slope gives the value of K, the proton association constant [equation (1)].

$$[Ni(S_2N_2H)_2] + H^+ \longrightarrow [Ni(S_2N_2H_2)(S_2N_2H)]^+ \quad \log K = 3.3 \qquad (1)$$

Reaction between S_4N_4 *and* Ni^{2+} *in dmso*.—When an excess of Ni^{2+} (10^{-2} mol dm^{-3}) was added to a 10^{-3} mol dm^{-3} S_4N_4 solution in dmso nothing was observed immediately. After several days the solution began to develop a violet colour which intensified progressively and reached a maximum absorbance after 14 d. The absorption spectrum of this solution is compared with that of $Ni(S_2N_2H)_2$ in Fig. 2. It is apparent that Ni^{2+} reacts with S_4N_4, although very slowly, to give the metal complex [$Ni(S_2N_2H)_2$]. The reaction is not quantitative despite the excess of metal ion (yield 45% based on S_4N_4). The formation of [$Ni(S_2N_2H)_2$] is accompanied by a slight acidification of the solution, to give a final pH of 3.7.

The ^1H and ^{15}N NMR spectra of this solution (Fig. 3) are very similar to the corresponding spectra of acidified solutions of [$Ni(S_2N_2H)_2$]. Broadening and shifting of the signals is caused by the excess of free paramagnetic Ni^{2+}. We can conclude that the reaction of S_4N_4 with Ni^{2+} in dmso leads to protonated complex rather than neutral [$Ni(S_2N_2H)_2$] a fact unnoticed in the spectrophotometric study. The relative intensity of the two signals in the ^1H NMR spectrum indicates that the degree of protonation must be significant.

We have examined the effect on the reaction of the addition of a base which neutralizes the liberated protons. An excess of potassium hydrogenphthalate increases the reaction rate significantly, as well as the extent of its completion (55% yield). Maximum absorbance is reached within 6 d. This effect is more dramatic when stoichiometric amounts of sodium acetate or tetrabutylammonium hydroxide are added. The reaction is almost completed in 24 h and the yield increases to 70%.

The nature of the solvent is a determining factor on the interaction of Ni^{2+} and S_4N_4 in solution. Methanol, the solvent used in the synthesis of this metal complex, is effective when heating at refluxing temperature, but at room temperature the reaction does not occur at all. Completely negative results were also obtained with acetone, acetonitrile, tetrahydrofuran, dimethylformamide, dioxane and sulpholane (tetrahydrothiophene 1,1-dioxide).

Solutions of S_4N_4 *in dmso. Formation of the Active Species* X_{345}.—The slowness of the reaction between Ni^{2+} and S_4N_4 at room temperature is easily understood taking into account that it is not a simple reaction. As stated in the introduction, it involves fragmentation, reduction and protonation of S_4N_4 to give the co-ordinated ligand $S_2N_2H^-$. How does this complex process occur? The metal ion could interact with S_4N_4 to give a complex of S_4N_4 which then reacts with the solvent.

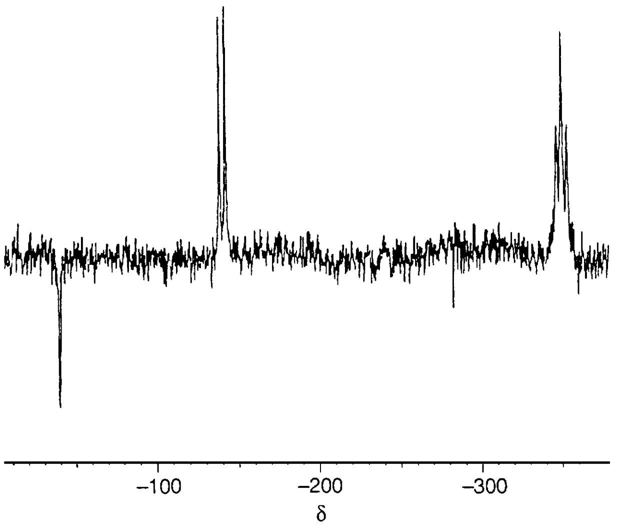
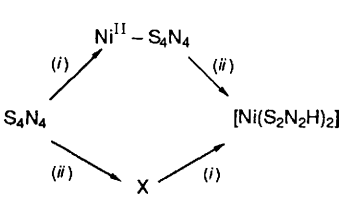


Fig. 3 Proton-coupled ^{15}N NMR spectrum of a solution of the reaction product between $S_4{}^{15}N_4$ (10^{-2} mol dm^{-3}) and Ni^{2+} (10^{-1} mol dm^{-3})



Scheme 1 (*i*) Ni^{2+}; (*ii*) solvent

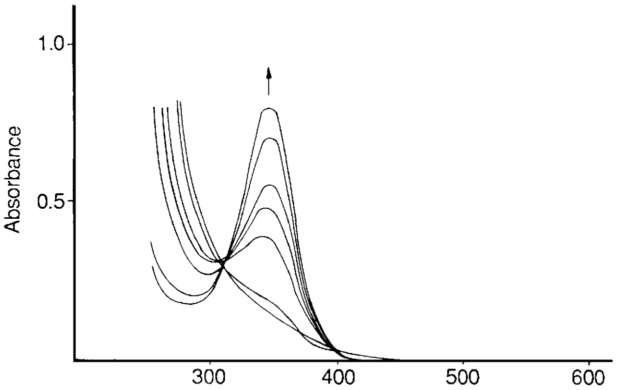


Fig. 4 Evolution with time of the absorption spectrum of 10^{-3} mol dm^{-3} S_4N_4. The last spectrum was recorded 14 d after the preparation of the solution (l = 0.1 cm)

Alternatively S_4N_4 could react first with the solvent forming an active species towards the metal ion (Scheme 1).

To provide insight into the nature of this reaction we have studied the behaviour of S_4N_4 solutions in dmso. Solutions of S_4N_4 in a variety of solvents have been obtained.[35] These solutions are not stable but, as far as we know, the decomposition reactions have never been studied.

We have recorded the absorption spectrum of a 10^{-3} mol dm^{-3} S_4N_4 solution in dmso following its evolution with time (Fig. 4). The initial spectrum changes very slowly with the appearance of an absorption band at 345 nm which progressively intensifies reaching its maximum absorption after 14 d. Associated with this spectral change the solution undergoes a slight acidification. It is evident that S_4N_4 solutions in dmso are not indefinitely stable, but develop into a different chemical species, X_{345}. Solutions of the latter are not stable either, but their decomposition rate is even slower than that of their formation.

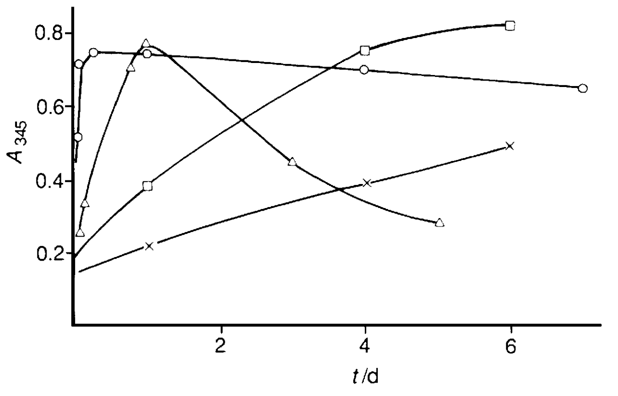


Fig. 5 Evolution with time of the absorbance at 345 nm of 10^{-3} mol dm^{-3} S_4N_4: (×) dmso solution, (○) 10^{-3} mol dm^{-3} sodium acetate in dmso, (□) 10^{-2} mol dm^{-3} potassium hydrogenphthalate in dmso and (△) dmso–water (80:20) solution

Addition of stoichiometric amounts (1:1) of sodium acetate to the solution increases the formation rate of X_{345} dramatically, the reaction being nearly complete after a few hours. However this is not all that happens. The addition of the base results in the instantaneous formation of a red colour which disappears after 1 h. Absorption spectra show a new band at 510 nm, much less intense than that of 345 nm, whose intensity quickly decreases with time. When the amount of sodium acetate is increased, the formation of X_{345} is still faster, but the decomposition rate also increases. The absorption at 345 nm decreases steadily. On the other hand the red species, although transitory, is formed in greater amounts. Similar results, although somewhat more pronounced, are obtained with tetrabutylammonium hydroxide instead of sodium acetate. We have observed no correlation between the decomposition rate of the red species and the formation rate of X_{345} and no absorption at 510 nm occurs when a base is added to a X_{345} solution. Thus we can conclude that these two species, detected spectrophotometrically, are formed directly from S_4N_4 in two different reactions. According to this the greater the transitory absorption at 510 nm, the less is the absorption at 345 nm.

The formation of X_{345} is optimized in the presence of an excess of potassium hydrogenphthalate. In this medium the maximum absorbance at 345 nm is reached within 6 d and the red species is not formed at all. On the other hand, acidification of a S_4N_4 solution in dmso inhibits the formation of X_{345} completely.

Actually the chemical species that reacts with S_4N_4 is not dmso but the traces of water it contains, as shown by the fact that addition of water greatly increases the formation rate of X_{345}. However under these conditions this species decomposes more quickly.

The absorption at 345 nm as a function of time for S_4N_4 solutions in different media is compared in Fig. 5.

We have studied S_4N_4 solutions in a variety of solvents and found in no case the formation of the absorption band at 345 nm. Methanol solutions decompose slowly at room temperature without displaying an absorption at about 345 nm, but interestingly this band is formed at refluxing temperature. However X_{345} is very unstable in this medium and decomposes quickly.

Interaction between the Active Species X_{345} *and* Ni^{2+}.—The results described above show that the rate of formation of the X_{345} species from the solutions of S_4N_4 in dmso almost coincides with the rate of formation of the metal complex $[Ni(S_2N_2H)_2]$ in the reaction between Ni^{2+} and S_4N_4. This suggests that in this last reaction S_4N_4 is not the true reagent but rather X_{345} which is formed by the reaction of S_4N_4 with the water in the solvent. To confirm this fact the direct interaction between X_{345} and Ni^{2+} has been studied. The results obtained

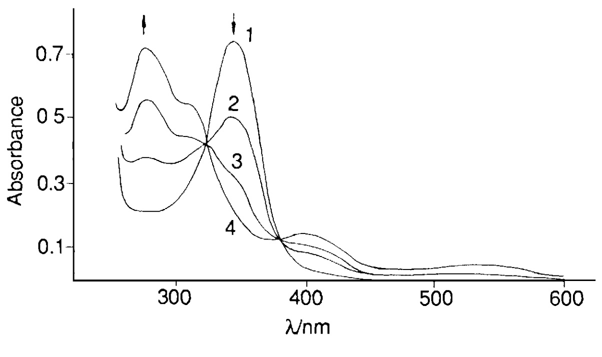


Fig. 6 Evolution with time of the absorption spectrum of a X_{345} solution after addition of an excess of Ni^{2+} (10^{-2} mol dm^{-3}): t = 0 (1), 1 (2), 3 (3) and 5 h (4); l = 0.1 cm

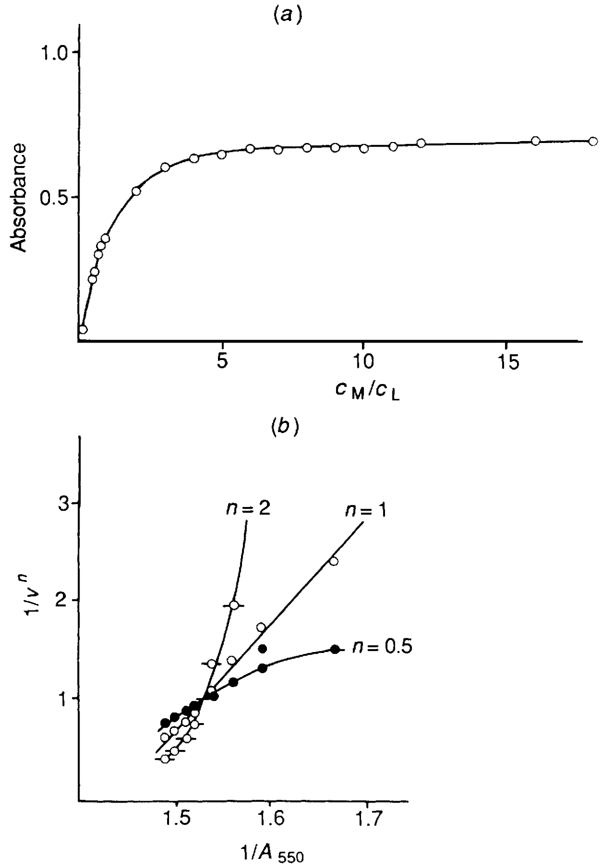


Fig. 7 Saturation curve (*a*) and Asmus plot (*b*) for the formation reaction of $[Ni(S_2N_2H)_2]$; c_M = total concentration of metal ion, c_L = total concentration of X_{345}; v = volume of metal-ion solution, n = stoichiometric coefficient

when using an excess of the metal ion (1:10 ratio) are shown in Fig. 6. In the absorption spectra a progressive decrease of the absorption at 345 nm is observed whereas the absorption bands of the metal complex appear and intensify. Under these conditions the reaction is completed in 5 h, and the band at 345 nm disappears completely. Two isobestic points at 380 and 320 nm indicate that only two absorbing species, X_{345} and the final nickel(II) complex, exist in the solution (Fig. 6). Associated with the formation of $[Ni(S_2N_2H)_2]$ a significant acidification of the solution occurs. It is then evident that X_{345} is the active species which reacts with Ni^{2+} ions in dmso as solvent. The formation process from S_4N_4 and Ni^{2+} can be summarized as in equation (2). Our results indicate that X_{345} is not the $S_2N_2H^-$ ligand itself but a different species. The reaction between X_{345} and Ni^{2+} is not instantaneous and it is not reversible. Once the complex has been formed its dissociation in an acid medium to regenerate X_{345} is not possible. Therefore the reaction is not just the formation equilibrium of a metal complex in solution but must involve a non-reversible transformation of the active species X_{345}.

$$S_4N_4 \xrightarrow{H_2O} X_{345} \xrightarrow{Ni^{2+}} [Ni(S_2N_2H)_2] \qquad (2)$$

The formation of $[Ni(S_2N_2H)_2]$ from S_4N_4 supposes that in some step of the reaction the tetramer cluster S_4N_4 is fragmented in two halves. When does this dissociation occur, during the formation of X_{345} or in its reaction with Ni^{2+}? A simple spectrophotometric study of the stoichiometry of the reaction can answer this question, since if X_{345} is a tetramer like S_4N_4 its interaction with Ni^{2+} must involve a 1:1 stoichiometry, whereas if it is dimeric the stoichiometry must be 2:1. Asmus' method[36] has been chosen because it does not require previous knowledge of the accurate concentration of the reagents as in our case. The linear Asmus plot in Fig. 7(*b*) clearly shows that the stoichiometry is 1:1. Therefore we may conclude that X_{345} retains the tetramer nature of S_4N_4.

Characterization of the Active Species.—Isolation of X_{345} to be characterized by X-ray diffraction seems somewhat problematic, as it is formed at very low concentrations and in a non-volatile solvent. Without discarding future attempts in this sense, we report here the results obtained for the characterization of X_{345} in solution using different experimental techniques.

Molecular exclusion chromatography and ion exchange. Elution experiments of S_4N_4 and X_{345} on Sephadex G-10 give nearly identical elution volumes for both species, indicating a very similar molecular weight. Thus we can conclude, in agreement with the spectrophotometric results described above, that the molecule of S_4N_4 is not fragmented during the formation of X_{345}.

The compound X_{345} is quantitatively and reversibly retained by an anion-exchange resin in the chloride form. This is accompanied by an acidification of the solution. These results indicate that X_{345} behaves as a weak acid, turning into an anionic form upon deprotonation. Both forms display the same absorption band at 345 nm.

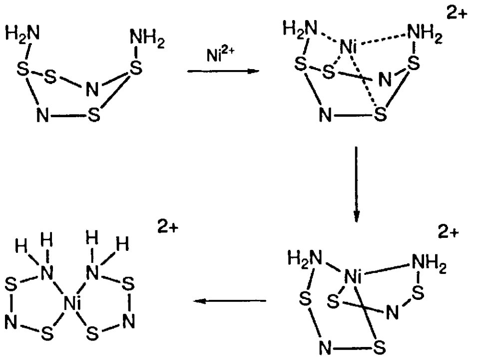
Infrared spectra. A freshly prepared solution of S_4N_4 in dmso displays only two IR bands in the 700–400 cm^{-1} range at 700 and 650 cm^{-1}, which are characteristic of the solvent. A new band slowly appears at 618 cm^{-1} and intensifies progressively. This band appears exactly in the same position when $S_4{}^{15}N_4$ (99% ^{15}N) is used, allowing its assignment to an S–S vibration. An S–N vibration should undergo an observable shift to lower frequencies.[37] The band disappears when Ni^{2+} is added to the solution, with the formation of $[Ni(S_2N_2H)_2]$. These results suggest that there are S–S bonds in X_{345} and that these bonds are broken in the interaction with Ni^{2+} ions.

Nuclear magnetic resonance. The proton NMR spectrum of X_{345} displays a rather intense peak at δ 7.1 and another weaker one at δ 11.6 (relative intensities *ca*. 10:1). Both signals, which reveal the existence of N–H bonds, are unambiguously assigned to X_{345} since both the absorption band at 345 nm and the two peaks in the ^1H NMR spectrum disappear completely when this species decomposes (after standing for several months). Moreover, the retention of X_{345} by an anion-exchange resin is accompanied by the disappearance of the two peaks in the NMR spectrum of the solution. This spectrum is very similar to that of the protonated metal complex $[Ni(S_2N_2H_2)(S_2N_2H)]^+$ (see Table 1), suggesting a close relation between the $S_2N_2H_2$ ligand and X_{345}.

The ^{15}N NMR spectrum of X_{345} shows a very sharp intense signal at δ −358 and two others, much weaker at δ −285 and at −95, respectively. When the spectrum is recorded at 55 °C the signal at δ −285 disappears and a new one appears at δ −159, which suggests some exchange phenomenon. No splitting of signals is observed in the proton-coupled spectrum, but under

Table 1 Proton and ^{15}N NMR data for nickel(II) complexes and X_{345}

		$[Ni(S_2N_2H)_2]$	$[Ni(S_2N_2H_2)(S_2N_2H)]^+$	X_{345}
^1H	NH	10.8	11	11.6
	NH_2	—	7.1	7.1
^{15}N	N=S	−39	−39	−95
	NH	−144	−144	−159 (55 °C)
	NH_2	—	−352	−358



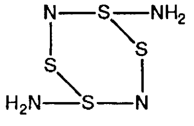
Scheme 2

these conditions the signal at δ −285 is not observed. This spectrum is compared with that of $[Ni(S_2N_2H_2)(S_2N_2H)]^+$ in Table 1.

The nature of the active species: $S_4N_2(NH_2)_2$. The molecule of X_{345} must contain four nitrogen atoms and four sulphur atoms, as evidenced by spectrophotometric and gel filtration data. The NMR study shows that the bidentate ligands S=N–S–NH_2, which are generated from X_{345}, must be practically preformed in this species and the IR spectrum shows the existence of S–S bonds. Then, we can identify our active species X_{345} with the compound $S_4N_2(NH_2)_2$, a novel S–N heterocycle with two exocyclic NH_2 groups **3**. This species behaves as a weak acid and will be slightly dissociated in solution [equation (3)].

$$S_4N_2(NH_2)_2 \rightleftharpoons [S_4N_2(NH_2)(NH)]^- + H^+ \quad (3)$$

The existence of S–N heterocycles of this kind is not completely unknown. The $[S_3N_2(NH_2)]^+$ cation has been isolated and structurally characterized.[38] It consists of a five-membered ring with a sulphur–sulphur bond and a NH_2 group bonded to one sulphur atom.



3

On the basis of the Lewis structure and the construction of a molecular model we propose the following molecular structure for the $S_4N_2(NH_2)_2$ molecule: a non-planar S_4N_2 six-membered ring with two exocyclic NH_2 groups linked to sulphur atoms and oriented towards the same face of the ring (Scheme 2). This structure allows us to visualize how the interaction with nickel(II) ions might occur.

In the first step Ni^{2+} would form a tetrahedral complex co-ordinating to $S_4N_2(NH_2)_2$ through the two nitrogen atoms of the NH_2 groups and two sulphur atoms of the ring. As a result of this interaction the S–S bonds would break and the S–N heterocycle would be fragmented into two $S_2N_2H_2$ units that remain co-ordinated as bidentate ligands (Scheme 2). At the same time, the co-ordination to the metal ion enhances the acidity of the NH_2 groups which deprotonate partially yielding the observed acidification of the solution [equation (4)].

$$[Ni(S_2N_2H_2)_2]^{2+} \rightleftharpoons [Ni(S_2N_2H_2)(S_2N_2H)]^+ + H^+ \quad (4)$$

On the Nature of the Formation Reaction of $S_4N_2(NH_2)_2$.—The formation of $S_4N_2(NH_2)_2$ implies a four-electron reduction of S_4N_4. In this reaction the eight-membered ring collapses into a six-membered ring through the breaking of two S–N bonds and the formation of two S–S bonds [equation (5)].

$$S_4N_4 + 4H^+ + 4e^- \longrightarrow S_4N_2(NH_2)_2 \quad (5)$$

The water contained in the dmso solvent is the reducing agent and hence it must be oxidized. Water oxidation could lead to O_2, H_2O_2 or OH$^•$ radicals. At first glance, the reaction seems unlikely given the strongly oxidizing nature of these species. However, in the last few years a number of experimental results have been accumulated, suggesting that OH^- anion can be an effective one-electron reductant in solvents such as acetonitrile and dmso.[39] The OH$^•$ radical that is produced may be captured by the solvent affording a free-energy change favourable enough to make the total redox reaction spontaneous. It is well known that OH radicals react very rapidly with dmso.[40]

Accordingly, we have observed that addition of OH^- anions to an S_4N_4 solution in dmso gives rise to the fast formation of $S_4N_2(NH_2)_2$. In this solvent OH^- is a very effective nucleophile and can also result in the degradation of S_4N_4 in another way causing the formation of the transient red species absorbing at 510 nm.

The redox reaction also occurs, although slowly, in the absence of OH^-, suggesting that water can also be a one-electron donor. There are other data that support the behaviour of water as a reductant in dmso solutions. Thus iron(II) complexes $[Fe(H_2vi)_3]^-$ and $[Fe(phen)_3]^{2+}$ are formed in the reaction of Fe^{3+} with violurate anions [violuric acid (H_3vi) = 1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime][41] and 1,10-phenanthroline,[42] respectively.

It should be noted that $S_4N_2(NH_2)_2$ is an isomer of the well known compound $S_4(NH)_4$. The latter molecule is produced by the $4e^-$ reduction of S_4N_4 with hydrated $SnCl_2$,[28] *i.e.* by the same overall process represented in equation (5) for the formation of $S_4N_2(NH_2)_2$. As Sn^{II} is a two-electron reductant the mechanism of the reaction must be different, resulting in a different product.

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