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A Microcalorimetric Determination of the Enthalpies of Formation in Solution of Nickel(II) Complexes with Tetraaza Macrocyclic Ligands of Varying Size

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The enthalpies of formation of nickel complexes with tetraaza macrocyclic ligands of varying ring size, from 12 to 15 members, have been determined by destroying the complexes in aqueous solution with alkaline cyanide. The octahedral–square-planar equilibria have been investigated, and the results are presented as $\Delta H°$ for both octahedral, blue and, when possible, square-planar, yellow species. Like the Cu(II) system, the blue, octahedral series exhibits a maximum in $\Delta H°$ with [14]aneN_4. This is discussed in terms of the relative size of the ligand and the metal ion. The unexpected reversal of $\Delta H°$ for the two square-planar complexes is rationalized in terms of expected ligand transformations.

Introduction

Direct calorimetric measurements, previously made in this laboratory,[1-3] of the enthalpies of formation of Cu(II) and Zn(II) complexes with saturated tetraaza macrocyclic ligands have highlighted the importance of matching the size of the aperture in the ligand with the size of the metal ion in order to maximize the enthalpy change. For Ni(II), however, the formation of the macrocyclic complexes is too slow to allow a parallel direct measurement of the enthalpies of formation, and so we have developed a method, based on the destruction of the metal complexes with a strongly alkaline cyanide solution, to give a quantitative yield of $[Ni(CN)_4]^{2-}$. ΔH for the nickel(II) complex with 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4) determined by this calorimetric method[4] proved to be 11 kcal·mol^{-1} less than the value previously reported[5] on which much of the early discussion on the origins of the macrocyclic effect had been based.

In this work we are now reporting the enthalpies of formation of Ni(II) complexes with three other tetraaza macrocyclic ligands containing from 12 to 15 members (Figure 1). Where possible, values are reported for both the blue octahedral species and the yellow square-planar species since the solution equilibria of these species have been separately studied spectrophotometrically (Table I).[6-8]

We are now able to assess further the extent to which both the geometrical features of the ligand and the size of the metal ion separately influence the enthalpies of formation and to make a comparison with the Cu(II) system by using the same ligands.

Experimental Section

Ligand and Complexes. [12]aneN_4·4HCl was prepared by the published method[9] and recrystallized from aqueous ethanol. The ligand [13]aneN_4 was synthesized through the condensation of the appropriate tosylated segments in alkaline solution, following the procedure published by Richman and Atkins.[9] The ligand [15]aneN_4 was a Strem Chemicals product, further purified as the tetrakis(hydrochloride) by bubbling HCl through an ethanolic solution of the ligand and recrystallized from aqueous ethanol. All the nickel(II) complexes of the above ligands ($NiL(ClO_4)_2$) were obtained by mixing equimolar solutions of $Ni(ClO_4)_2·6H_2O$ and the ligand in hot butanol and recrystallizing the product from ethanol. Elemental analyses were as follows. Anal. Calcd for [12]aneN_4·4HCl: C, 30.2; H, 7.6; N, 17.6. Found: C, 29.9; H, 7.9; N, 17.6. Calcd for [13]aneN_4: C, 58.0; H, 11.9; N, 30.1. Found: C, 57.8; H, 12.2; N, 30.4. Calcd for [15]aneN_4·4HCl: C, 36.7; H, 8.4; N, 15.6. Found: C, 36.4; H, 8.7; N, 15.5. Calcd for Ni([12]aneN_4)$(ClO_4)_2$: C, 22.4; H, 4.7; N, 13.0. Found: C, 22.9; H, 5.0; N, 13.4. Calcd for Ni([13]aneN_4)$(ClO_4)_2$: C, 24.4; H, 5.2; N, 12.6. Found: C, 24.1; H, 5.1; N, 12.5. Calcd for Ni([15]aneN_4)$(ClO_4)_2$: C, 28.0; H, 5.6; N, 11.9. Found: C, 27.7; H, 5.4; N, 11.7. Calcd for $K_2[Ni(CN)_4]$: C, 19.9; N, 23.3. Found: C, 19.8; N, 23.3.

Table I. Enthalpy Changes of the Blue (High-Spin) to Yellow (Low-Spin) Conversion and Percentages of Each Species at Equilibrium (25 °C) in Aqueous Solution

L	$\Delta H°$, kcal·mol^{-1}	% high-spin form	% low-spin form	ref
[12]aneN_4		99		8
[13]aneN_4	7.5	13	87	8
[14]aneN_4	5.4	29	71	6
[15]aneN_4		99		8

Other Reagents. $K_2[Ni(CN)_4]·3H_2O$ was prepared by the published method[10] and dehydrated to constant weight at 100 °C to give anhydrous $K_2Ni(CN)_4$. Alkaline cyanide solutions (0.1 M) were prepared by adding appropriate quantities of NaOH (Erba RP reagent) and NaCN (Erba RP reagent) to CO_2-free, twice-distilled water.

Apparatus. An LKB Batch microcalorimeter (10700-2) was used for all the calorimetric measurements. A full description of this apparatus, its calibration, and its mode of operation for slow reactions has already been given in detail.[4] UV spectral measurements were made on a Varian Cary 17 spectrophotometer equipped with 1-mm path length quartz cells.

Calorimetric Procedure. The reactions for which $\Delta H°$ has been determined can be represented by the general equation

$$\underset{(0.01-0.02\ M)}{NiL^{2+}} + \underset{(0.1\ M\ \text{in}\ 0.9\ M\ NaOH)}{4CN^-} \rightleftharpoons [Ni(CN)_4]^{2-} + L \qquad (1)$$

where L = [12]aneN_4, [13]aneN_4, and [15]aneN_4; values of $\Delta H°$ for L = $(H_2O)_6$ and [14]aneN_4 have been reported previously.[4] In a typical calorimetric measurement 0.4 cm^3 of the nickel complex solution was introduced by weight into one side of the calorimetric cell compartment; 2.5 cm^3 of the NaOH/NaCN solution (0.9 M NaOH, 0.1 M NaCN) was introduced into the other by a precision pipet (PIPETMAN). The calorimeter was allowed to equilibrate overnight until a steady base line was obtained on the most sensitive range. Just before the measurements were started, the sensitivity was decreased and the reaction started by mixing the reactants. As the reaction proceeded, the heat output decreased and the sensitivity was increased. The reaction was considered complete when no further

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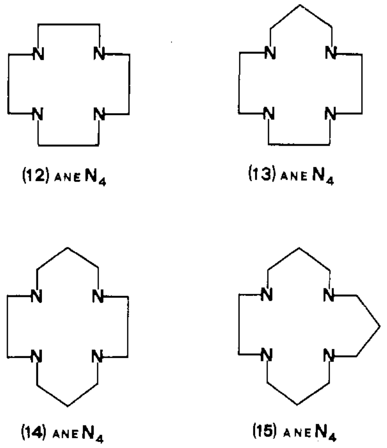

Figure 1.

Table II. $\Delta H°$ for the Reaction $[NiL]^{2+}(aq) + 4CN^-(aq) \rightarrow [Ni(CN)_4]^{2-}(aq) + L(aq)$[a]

L	$-\Delta H°$(25 °C), kcal·mol^{-1}	L	$-\Delta H°$(25 °C), kcal·mol^{-1}
[12]aneN$_4$	30.6	[15]aneN$_4$	24.9
	30.7		24.7
	31.3		25.3
	30.9		24.6
	mean 30.9 ± 0.3		mean 24.9 ± 0.3
[13]aneN$_4$	29.0		
	29.6		
	29.3		
	29.3		
	29.1		
	mean 29.3 ± 0.2		

[a] $\Delta H°$ for the reaction $Ni^{2+}(aq) + 4CN^-(aq) \rightarrow Ni(CN)_4{}^{2-}(aq)$ is −42.8 kcal·mol^{-1}.[4]

heat effect could be detected on the original highest sensitivity range and the base line had the same value as before the reaction. Different ligands displayed different kinetic inertness and the reaction time varied as follows: Ni^{2+}(aq), 0.5 h;[4] [Ni([12]aneN$_4$)]$^{2+}$, 0.6 h; [Ni([13]aneN$_4$)]$^{2+}$, 0.6 h; [Ni([14]aneN$_4$)]$^{2+}$, 5 h;[4] [Ni([15]aneN$_4$)]$^{2+}$, 4 h.

In order to confirm that the reaction was complete and that equilibrium had been reached, we determined the concentration of $[Ni(CN)_4]^{2-}$ spectrophotometrically in the reaction mixture, immediately following the collection of the thermal data. This was done by using the sharp absorption band at 268 nm ($\epsilon = 1.21 \times 10^4$ dm^3 cm^{-1} mol^{-1}), and in each case the concentration of $[Ni(CN)_4]^{2-}$ was close to the equilibrium value expected: ~98%. Although some 2% of the species $[Ni(CN)_5]^{3-}$ is expected in the equilibrium mixture, no correction was made to the experimental data since it has been shown previously that this amounts to less than 0.2%.[4] However, a correction for the enthalpy of dilution of the NaOH/NaCN solution was made to each measurement by introducing 2.5 cm^3 of NaOH-/NaCN solution into one side of the mixing cell and pure water (0.4 cm^3) into the other. The reaction cells were coated with paraffin wax to prevent creeping, this wax coating being renewed after 10–15 determinations.

Results and Discussion

Nickel(II) complexes with macrocyclic ligands are known to exist in aqueous solution as mixtures of the high-spin (blue) and low-spin (yellow) forms:

$$\begin{array}{cc} [NiL(H_2O)_2]^{2+} \rightleftharpoons & [NiL]^{2+} + 2H_2O \\ \text{high spin,} & \text{low spin,} \\ \text{blue (octa-} & \text{yellow (square} \\ \text{hedral)} & \text{planar)} \end{array}$$

These equilibria have been studied,[6-8,11] and the relative percentages of each form present at 25 °C are reported in Table I together with the enthalpy change for the blue → yellow conversion, which has been obtained from equilibrium data over a range of temperature. The experimental results for reaction 1 with the different ligands are given in Table II. Enthalpies of formation of the nickel complexes were determined by using the values of the enthalpy of formation of $[Ni(CN)_4]^{2-}$ reported in ref 4. These enthalpies of formation, which refer to the equilibrium mixture at 25 °C, were then converted by using the $\Delta H°$ values for the blue → yellow conversion and are reported in Table III as the enthalpies of formation of the blue and yellow forms.

Table III. Formation in Aqueous Solution at 25 °C of High-Spin and Low-Spin Nickel(II) Complexes with Tetraaza Macrocycles: Enthalpy Changes (kcal·mol^{-1}) for the Reaction $Ni^{2+}(aq) + L(aq) \rightarrow NiL^{2+}(aq)$

complex	reacn mix	high-spin form	low-spin form
[Ni([12]ane)N$_4$]$^{2+}$	11.9 ± 0.3[a]	11.9	
[Ni([13]ane)N$_4$]$^{2+}$	13.5 ± 0.3[b]	20.0	12.5
[Ni([14]ane)N$_4$]$^{2+}$	20.3 ± 0.2[c,d]	24.1	18.7
[Ni([15]ane)N$_4$]$^{2+}$	17.9 ± 0.3[a]	17.9	

[a] More than 99% of the high-spin form. [b] 87% of low-spin form. [c] 71% of the low-spin form. [d] Reference 4.

Blue (Octahedral), High-Spin Complexes. $\Delta H°$ is largest for the complex [Ni([14]aneN$_4$)]$^{2+}$. Busch et al.[12] have calculated the ideal M–N bond distances for these ligands, by minimizing the configurational energy when the four donor nitrogen atoms are constrained in a planar arrangement at the corners of a square. These ideal M–N distances[12] are as follows: [12], 1.81 Å; [13], 1.92 Å; [14], 2.07 Å; [15]aneN$_4$, 2.22 Å.

Experimentally, M–N distances found in octahedral blue polyamine complexes lie in the range 2.05–2.10 Å[13-15] and suggest that, of these ligands, [14]aneN$_4$ can most satisfactorily accommodate a Ni(II) in an octahedral geometry while remaining in a state of minimum strain.

The larger ligand [15]aneN$_4$ prefers a larger cation than Ni(II) to remain in this minimum strain state. With Ni(II) it is most probable that the behavior will parallel that observed for Cu(II), where a crystal structure determination[16] has shown that the ligand contracts, resulting in a less favorable flattened ring conformation.

We would therefore expect a similar reduction in the enthalpy of formation of the complex with [15]aneN$_4$ relative to that with [14]aneN$_4$ in keeping with the observed values of 24.1 and 17.9 kcal·mol^{-1}.

Spectroscopically, the $10Dq^{xy}$ value for the complex with [15]aneN$_4$[17] is less than that with [14]aneN$_4$, illustrating the weaker in-plane interactions between metal and ligand.

In contrast, complexes with the two smaller ligands [12]aneN$_4$ and [13]aneN$_4$ have ideal M–N bond distances of 1.81 and 1.91 Å,[12] which are smaller than those observed in octahedral nickel polyamine complexes. Several possibilities are available to relieve this situation; the ligand can fold resulting in a cis-octahedral complex or the complex can become five-coordinate with the metal ion positioned above the plane of the four donor nitrogen atoms. Again, in either case a decrease

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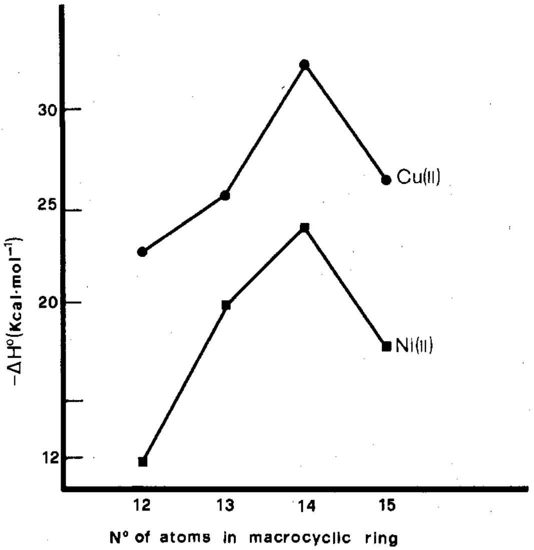

Figure 2. Enthalpy changes for the reaction $M^{2+}(aq) + L(aq) \rightarrow ML^{2+}(aq)$ in water at 25 °C (M = Ni, Cu; L = 12- to 16-membered tetraaza macrocycles).

in $\Delta H°$ would be expected: in the first because of increased configurational interactions in the higher energy folded configuration of the ligand and in the second both from a reduction in the number of bonds to the nickel and from a loss in their effectiveness due to the removal of the d ion from the plane containing the four donor nitrogen atoms. Cis-octahedral coordination is suggested for both nickel complexes from spectroscopic studies both in the solid state and in solution.[8,17,18]

Yellow (Square-Planar), Low-Spin Complexes. The conversion of an octahedral blue nickel complex to the square-planar yellow form is accompanied by a sharp reduction in the Ni–N bond distance. Typically, Ni–N distances in yellow, low-spin tetraamine complexes lie in the range 1.86–1.92 Å,[15,19,20] some 0.2 Å less than in equivalent octahedral blue complexes. It would seem that $\Delta H°$ should reach a maximum with [13]aneN_4 (ideal M–N distance 1.92 Å). In this series, experimental results are only available for complexes with [13]aneN_4 and [14]aneN_4, since the percentages of the yellow form for [12]aneN_4 and [15]aneN_4 in the equilibrated solution at 25 °C are negligible. However, $\Delta H°$ for $[Ni([14]aneN_4)]^{2+}$ exceeds that of $[Ni([13]aneN_4)]^{2+}$ by 6.2 kcal·mol^{-1}, and it is not sufficient in this case to consider only the relative size of the metal ion and the aperture in the ligand. Unlike the case for the high-spin complexes where the geometry can vary considerably, for a nickel(II) complex in the low-spin state the four donor nitrogen atoms must be coplanar. However, this square-planar requirement introduces a relatively greater degree of internal strain in coordinated [13]aneN_4 compared to [14]aneN_4. In other words, coordinated [14]aneN_4 with four coplanar nitrogens, adopts a configuration which is more or less strain free and similar to that adopted by the ligand itself. While the configuration of the ligand in the case of [13]aneN_4 is not known, it is highly probable that it can adopt a configuration much less strained than that demanded by the geometrical constraints of a square-planar complex. We believe it is this necessity to adopt a more strained configuration in the complex than in the free ligand itself, which is responsible for the much lower $\Delta H°$ for $Ni[([13]aneN_4)]^{2+}$ and which outweighs any small advantage for which the more exact matching of sizes of ion and ligand would have been responsible.

Comparison with Copper(II) Complexes. The enthalpies of formation of copper(II)[3,21] and high-spin nickel(II) complexes with these ligands are compared in Figure 2. The same overall trend is observed in both series with a maximum enthalpy of formation with [14]aneN_4. This is to be expected since observed Cu–N bond lengths (2.03–2.10 Å) in polyamine complexes are almost exactly the same as the observed range for Ni–N bonds (2.05–2.10 Å). It is possible to look rather more closely at these results and make a more refined interpretation. For complexes with [14]aneN_4 and [15]aneN_4, the difference in $\Delta H°$ between Cu(II) and Ni(II) is the same (8.4 and 8.6 kcal·mol^{-1}). For these two cases we can make a realistic comparison since the geometries of both the copper and nickel complexes are the same (trans octahedral)[16,23] and the lower $\Delta H°$ for the nickel is consistent with other known comparisons between copper(II) and nickel(II) complexes.[22] For [12]aneN_4, the copper complex adopts a square-pyramidal structure[24] in which the conformation of the ligand is identical with that predicted for the free ligand, whereas for the nickel complex a cis-octahedral complex is predicted from spectroscopic considerations.[18] This ligand is therefore much more likely to be in a less favorable conformation in the nickel complex, resulting in a greater difference in $\Delta H°$ between copper and nickel of 10.8 kcal·mol^{-1}.

For [13]aneN_4 however this $\Delta H°$ difference is reduced to 5.6 kcal·mol^{-1}. In this case, there is spectroscopic evidence[17] for a cis-octahedral arrangement in the nickel complex, and it therefore seems, in view of this small difference in $\Delta H°$, that in the copper complexes the ligand would be likely to adopt a more strained conformation which would be approximately planar rather than to adopt a strain-free five-coordinate geometry.

Scaled Ideal M–N Distances and the Interpretation of the Complexation Enthalpies. The previous interpretation of the trend of the enthalpies of formation of the high- and low-spin Ni(II) complexes with 12- to 16-membered tetraaza alkanes was essentially based on the more or less favorable match between the size of the metal ion and the aperture of the macrocycle. In this connection the concept of "absolute ideal M–N distance"[12] was used. It has been pointed out by Professor Busch that these values are probably too large and should be scaled to the following series of values: [12], 1.70 Å; [13], 1.80 Å; [14], 1.94 Å; [15], 2.08 Å. According to this new sequence, the 15-membered ligand, rather than the 14-membered one, would fit Ni^{2+}(high spin) perfectly; in this situation, the lower complexation exothermicity found for [15]aneN_4 with respect to [14]aneN_4 must be totally ascribed to the particularly unfavorable "strain energy" experienced by the former macrocycle. On the other hand, for the low-spin Ni(II) complexes, it is the 14-membered ligand that fits the metal ion better than the 13-membered homologue, accounting for the more exothermic complexation in water.

It is clear that the two possibilities, based on the different series of "ideal M–N distances", "absolute" and "scaled", are specular and equally rational, and we are not in a position to make the final choice. The second possibility assumes that [15]aneN_4 is the tailor-made ligand for the ideal coplanar coordination of high-spin Ni(II). No structural data have been reported on this complex. However, an X-ray study has been

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recently carried out[16] on the corresponding coplanarly coordinated complex of copper(II) (this ion has approximately the same size as high-spin Ni(II)). It is seen that the 15-membered macrocycle is quite distorted in its coordinative arrangement; in particular, one of the six-membered rings is forced to adopt the particularly unfavorable "sofa" configuration.

Acknowledgment. We thank Dr. R. M. Clay for helpful discussion. We are indebted to Professor D. H. Busch, who, as a referee, suggested a possible interpretation of the complexation enthalpies, based on the "scaled ideal M–N distances".

Registry No. $[Ni([12]aneN_4)(OH_2)_2]^{2+}$, 71901-52-5; $[Ni([13]aneN_4)(OH_2)_2]^{2+}$, 71928-49-9; $[Ni([13]aneN_4)]^{2+}$, 53277-10-4; $[Ni([14]aneN_4)(OH_2)_2]^{2+}$, 64616-26-8; $[Ni([14]aneN_4)]^{2+}$, 46365-93-9; $[Ni([15]aneN_4)(OH_2)_2]^{2+}$, 71901-51-4; $[12]aneN_4 \cdot 4HCl$, 10045-25-7; $[13]aneN_4$, 295-14-7; $[15]aneN_4 \cdot 4HCl$, 71888-10-3; $Ni([12]aneN_4)(ClO_4)_2$, 71911-56-3; $Ni([13]aneN_4)(ClO_4)_2$, 71901-50-3; $Ni([15]aneN_4)(ClO_4)_2$, 71882-19-4; $K_2[Ni(CN)_4]$, 14220-17-8.

Contribution from the Gesellschaft für Biotechnologische Forschung mbH, Braunschweig-Stöckheim,
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Bicyclic Sulfur–Nitrogen Compounds: Molecular Structures of *S*,*S*-Dimethylpentasulfur Hexanitride and 1-[*S*,*S*-Dimethyl-*N*-(trimethylsilyl)sulfodiimide]bicyclo[3.3.1]pentaazatetrathiane

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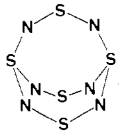
Pentasulfur hexanitride S_5N_6 and dimethylpentasulfur hexanitride $S_5N_6(CH_3)_2$ (**5**) may be prepared in high yield by the reaction of $S_4N_4Cl_2$ with $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ and $(CH_3)_3SiN{=}S(CH_3)_2{=}NSi(CH_3)_3$ (**4**), respectively. The observation of small quantities of S_5N_6 and S_4N_4 as byproducts in the latter reaction affords a rationalization of the formation of $S_5N_7Si(CH_3)_5$ (**6**) from the reaction of $S_3N_3Cl_3$ with **4**. A crystal structure analysis of **5** revealed a basket structure in which an $-N{=}S(CH_3)_2{=}N-$ unit bridges two sulfur atoms of an S_4N_4 cradle. **5** crystallizes orthorhombic, space group *Fddd*, with $a = 10.810$ (3) Å, $b = 10.698$ (2) Å, $c = 33.050$ (3) Å, $D_x = 1.91$ g cm^{-3}, and $Z = 16$. The structure was refined by full-matrix least squares to the terminal values $R = 0.054$ and $R_w = 0.049$ for 920 reflections with $I \geq 1.5\sigma(I)$. $S_5N_6(CH_3)_2$ contains a crystallographic diad axis with the $S(CH_3)_2$ groups disordered; i.e., the individual molecules do not display C_2 symmetry. Whereas the bonding in the S_4N_4 cradle is similar to that in S_5N_6 with transannular S···S distances of 2.433 (3) and 3.908 (3) Å, the S–N bonds of the handle are, at 1.643 (3) Å, much shorter than those in S_5N_6. **6** crystallizes triclinic, space group $P\bar{1}$, with $a = 12.026$ (3) Å, $b = 10.493$ (3) Å, $c = 6.810$ (2) Å, $\alpha = 90.12$ (2)°, $\beta = 108.81$ (2)°, $\gamma = 71.51$ (2)°, $D_x = 1.57$ g cm^{-3}, and $Z = 2$. The structure was refined by full-matrix least squares to the terminal values $R = 0.036$ and $R_w = 0.039$ for 2825 reflections with $I \geq 1.5\sigma(I)$. The structure of the neutral S_4N_5 unit displays an S_3N_3-ring containing the three sulfur atoms of coordination number 3, in which there is a high degree of π delocalization. This ring is bridged by an $-N{=}S{=}N-$ unit with N–S bonds of predominantly single and double bond character. Five S···S interactions are observed in the range 2.736–2.846 Å with the sixth 3.814 (1) Å.

Introduction

Very few bicyclic sulfur–nitrogen compounds are known. The only structurally characterized derivatives are the ions $S_4N_5O^-$,[2] $S_4N_5^+$,[3] and $S_4N_5^-$[4] and one neutral species S_5N_6,[5,6] which was reported recently. However, as a result of a lack of detailed understanding of most of their preparation reaction mechanisms, it has not previously proved possible to evolve a general route for the synthesis of this class of compounds. In this paper we report a facile synthetic route for the preparation of the bicyclic sulfur–nitrogen compounds S_5N_6 (**3**) and $S_5N_6(CH_3)_2$ (**5**) using $S_4N_4Cl_2$ (**1**) and respectively $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ (**2**) and $(CH_3)_3SiN{=}S(CH_3)_2{=}NSi(CH_3)_3$ (**4**) as starting materials. We have also recently published details of the preparation of the first neutral S_4N_5 derivative $S_4N_5N{=}S(CH_3)_2{=}NSi(CH_3)_3$ (**6**) from $S_3N_3Cl_3$ and **4**, the structure of which was established from its IR and ^1H NMR spectra. However, the course of this reaction could only now be established, on the basis of the byproducts S_5N_6 and S_4N_4 which may be isolated upon the reaction of **1** with **4**. We have furthermore carried out X-ray structural analyses on **5** and **6** in order to characterize the nature of the S–N bonding and to provide knowledge of the sulfur–sulfur interactions in these species.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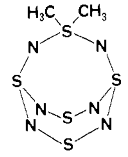
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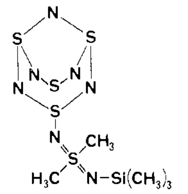
6

Experimental Section

NMR Spectra. Proton spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane used as external standard.

IR Spectra. Infrared spectra were recorded as both solution (CCl_4) and Nujol mulls on a Perkin-Elmer 157 spectrophotometer.

Mass Spectra. Mass spectra were recorded on a Varian CH 7 instrument operating at 70 eV.

Materials. All reactions were carried out in a dry nitrogen atmosphere with the necessary precautions being taken in the handling of air- and moisture-sensitive compounds. Solvents were purified by

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