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,
and the Anorganisch-Chemisches Institut der Universität, Frankfurt am Main, Federal Republic of Germany

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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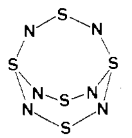
Received June 11, 1979

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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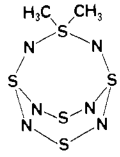
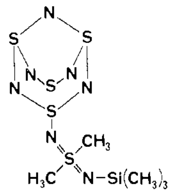


5



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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(1) (a) Gesellschaft für Biotechnologische Forschung mbH, Braunschweig-Stöckheim. (b) Anorganisch-Chemisches Institut der Universität Frankfurt am Main.

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Table I. Analytical Data for Compounds **3**, **5**, and **6**

compd		% C	% H	% N	% S
S_5N_6 (**3**)	calcd			34.43	65.57
	found			34.2	65.1
$C_2H_6N_6S_5$ (**5**)	calcd	8.75	2.21	30.63	58.41
	found	8.5	2.0	30.9	57.1
$C_5H_{15}N_7S_5Si$ (**6**)	calcd	16.61	4.19	27.12	44.34
	found	16.1	4.1	26.9	43.7

Table II. Mass Spectral Data for Compounds **3**, **5**, and **6**

compd	fragment	*m/e*	% intens
S_5N_6 (**3**)	M − NS	198	39
	S_4N_4	184	2
	S_3N_3	138	28
	S_3N_2	124	35
	S_2N_2	92	72
	NS_2	78	100
	S_2	64	11
	NS	46	100
$S_5N_6(CH_3)_2$ (**5**)	M	274	1
	M − NS	228	2
	$S_4N_5CH_3$	213	1
	S_4N_5	198	1
	S_4N_4	184	2
	$S_3N_3(CH_3)_2$	168	4
	S_3N_3	138	47
	S_3N_2	124	2
	S_2N_2	92	34
	NS_2	78	52
	NS	46	100
$S_5N_7Si(CH_3)_5$ (**5**)	M	361	1
	$S_4N_5Si(CH_3)_5$	301	5
	$S_4N_5(CH_3)_2$	228	1
	S_4N_4	184	2
	S_3N_3	138	16
	S_3N_2	124	7
	S_2N_2	92	34
	$Si(CH_3)_2$	73	100
	NS	46	80

Table III. Infrared Spectral Data (in cm^{-1}) of Compounds **3**, **5**, and **6**

S_5N_6 (**3**)	1085 ssh, 1063 s, 1028 s, 968 w, 940 s, 852 s, 832 m, 695 s
$S_5N_6(CH_3)_2$ (**5**)	3040 m, 1064 s, 1047 vs, 1027 s, 968 s, 960 s, 944 s, 860 s, 778 s, 738 m, 725 m, 695 m
$S_5N_7Si(CH_3)_5$ (**6**)	1430 w, 1415 w, 1400 m, 1340 m, 1318 w, 1275 s, 1258 s, 1075 m, 1030 m, 1020 m, 980 m, 950 m, 940 m, 920 s, 880 w, 855 s, 770 m, 760 m, 742 m, 722 m, 702 m, 680 m

Table IV. Experimental Details of the X-ray Diffraction Studies of **5** and **6**

	$S_5N_6(CH_3)_2$ (**5**)	$S_5N_7Si(CH_3)_5$ (**6**)
	Crystal Data	
fw	274.4	361.6
space group	*Fddd* (No. 70)	$P\bar{1}$ (No. 2)
unit cell consts (22 ± 1 °C)		
a, Å	10.810 (3)	12.026 (3)
b, Å	10.698 (2)	10.493 (3)
c, Å	33.050 (5)	6.810 (2)
α, deg	90	90.12 (2)
β, deg	90	108.81 (2)
γ, deg	90	71.51 (2)
Z	16	2
D_{calcd}, g cm^{-3}	1.91	1.57
	Measurement of Intensity Data	
radiation	Mo Kα	Cu Kα
scan mode	θ–2θ	θ–2θ
scan speed, deg min^{-1}	2.02–9.77	2.02–9.77
2θ angular range	$3° \leqslant 2\theta \leqslant 55°$	$3° \leqslant 2\theta \leqslant 145°$
reflctns measd	1062	2927
abs correctn, cm^{-1}	μ(Mo Kα) = 10.8	μ(Cu Kα) = 74.4
max transmisn	0.597	0.886
min transmisn	0.560	0.344
	Structure Refinement	
I observn criterion	$I \geqslant 1.5(I)$	$I \geqslant 1.5(I)$
no. of reflctns	920	2825
k (scale factor)	2.7930	1.0537
g (weighting factor)	0.0002	0.0002
largest shift/esd	−0.044	0.007
$R = (\Sigma \lvert F_o - F_c \rvert / \Sigma \lvert F_o \rvert)$	0.054	0.036
$R_w = (\Sigma w^{1/2} \lvert F_o - F_c \rvert / \Sigma w^{1/2} \lvert F_o \rvert)$	0.049	0.039
R (all reflctns)	0.062	0.037

conventional methods and handled under N_2 atmosphere. Reported procedures were employed to prepare the starting materials $S_4N_4Cl_2$[7] (**1**) and $(CH_3)_3SiNS(CH_3)_2NSi(CH_3)_3$[8] (**4**).

Preparation of Pentasulfur Hexanitride from $S_4N_4Cl_2$ (1) and $(CH_3)_3SiNSNSi(CH_3)_3$ (2). A solution of 0.9 g of **2** (0.004 mol) in acetonitrile (25 mL) was added dropwise under stirring over a period of 1 h to a solution of 1.0 g of **1** (0.004 mol) in acetonitrile (50 mL). The reaction mixture was then brought to room temperature and stirred for another 20 h. A bright yellow precipitate was collected upon filtering of the reaction mixture. An IR spectrum showed it to be a mixture of **3** and S_4N_4.

On washing of the precipitate repeatedly with small quantities of benzene (5 × 10 mL), S_4N_4 could be effectively removed and pure **3** (0.78 g, 81%) was obtained. The washing operations must be performed very quickly, otherwise the yield of **3** is diminished on account of its solubility in benzene. The filtrate of the reaction yielded only a small quantity of S_4N_4, on cooling to −70 °C.

Preparation of Pentasulfur Hexanitride (3) from $S_4N_4Cl_2$ (1) and $N[Sn(CH_3)_3]_3$. A 0.5-g sample of **1** (0.002 mol) was dissolved in 40 mL of acetonitrile and cooled to 0 °C under stirring. To this, a solution 1.0 g of $N[Sn(CH_3)_3]_3$ (0.002 mol) in acetonitrile (25 mL) was added dropwise over a period of 1 h. After complete addition, the contents of the reaction flask were brought to room temperature and stirred for another 24 h. By filtration of the reaction mixture, a deep yellow precipitate and an orange-red filtrate were obtained. The precipitate was washed with benzene (as in the above procedure) to remove S_4N_4. The residual yellow powdery solid was dried in vacuo to yield **3** (0.15 g, 32%). The filtrate of the reaction also yielded small amounts of S_4N_4 and **3** on cooling to −70 °C.

Preparation of *S*,*S*-Dimethylpentasulfur Hexanitride (5) from $S_4N_4Cl_2$ (1) and $(CH_3)_3SiNS(CH_3)_2NSi(CH_3)_3$ (4). A 1.28-g sample of **1** (0.005 mol) was dissolved in 40 mL of acetonitrile with stirring, and the mixture was cooled to 0 °C. A 1.18-g sample of **4** (0.005 mol) dissolved in 20 mL of acetonitrile was then added dropwise to this solution over a period of 1.5 h. After the addition was complete, the reaction mixture was allowed to reach room temperature and then stirred for another 14 h at this temperature and filtered off to obtain a bright yellow powdery solid. This was washed with acetonitrile (2 × 15 mL) and dried under vacuum to yield **5** (1.22 g, 88%). The initial yellow precipitate from the reaction was found to contain S_4N_4 as an impurity. From the filtrate of the reaction small amounts of **3**, **5**, and S_4N_4 were recovered on cooling to −70 °C. The ^1H NMR spectrum of **5** in acetonitrile solution gave a singlet at δ 3.26.

Caution! Both S_5N_6 and $S_5N_6(CH_3)_2$ are very explosive. During the melting point determination for S_5N_6, the apparatus was broken to pieces. Additionally a large glass funnel containing about 50 mg of S_5N_6 crumbled into powder while S_5N_6 was being removed from it in the drybox. Quartz combustion tubes used for CH determination of $S_5N_6(CH_3)_2$ also were broken. It is therefore recommended that these syntheses be carried out on a small scale (ca. 1 g) and that great care be exercised in the handling of these compounds.

Preparation of 1-[*S*,*S*-Dimethyl-*N*-(trimethylsilyl)sulfodiimide]-bicyclo[3.3.1]pentaazatetrathiane (6) from $S_3N_3Cl_3$ and 4. **6** was obtained, as previously published,[6] as one of the products of the reaction of thiatriazyl trichloride $S_3N_3Cl_3$ with **4**. After removal of the precipitate of $[S_4N_5(CH_3)_2]^+Cl^-$, yellow prismatic crystals of **6** were obtained upon cooling of the filtrate to −70 °C for a period of 2–3 days. Analytical, mass spectral, and IR data for compounds **3**, **5**, and **6** are summarized in Tables I–III.

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(7) L. Zborilova and P. Gebauer, *Z. Anorg. Allg. Chem.*, **448**, 5 (1979).
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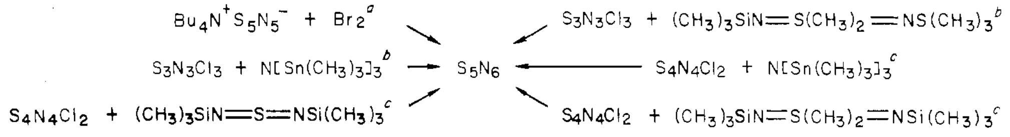
Scheme I



[a] Reference 5. [b] Reference 6. [c] This work.

Data Collection for 5 and 6. Experimental work was carried out on a Syntex P2$_1$ diffractometer, for **5** with graphite-monochromated Mo Kα radiation and for **6** with graphite-monochromated Cu Kα radiation. Details of the intensity data collection and structure refinement are given in Table IV. Unit cell dimensions were obtained by least-squares refinement of angular settings of 15 reflections $\pm(hkl)$ with $2\theta_{\mathrm{MoK}\alpha} > 20°$. Intensity data were collected in the θ–2θ mode to a maximum 2θ value of 55° for **5** and 145° for **6**. Two control reflections were monitored every 42 reflections. No significant deviations in their intensities were observed. The net intensities of each reflection were given by $I = [P - (\mathrm{B1} + \mathrm{B2})]S$, where P is the total scan count, B1 and B2 are the stationary left and right background counts, respectively, each measured for half of the total scan time, and S is the scan rate. The standard deviation of the net intensity is then defined as

$$\sigma(I) = [P + (\mathrm{B1} + \mathrm{B2})]^{1/2}S$$

Reflections were scanned from 0.8° below the Kα_1 to 0.8° above the Kα_2 2θ value. Absorption corrections were applied empirically on the basis of azimuthal scan data with ψ intervals of 20° for 15 strong reflections in various regions of reciprocal space. After reflections with $I < 1.5\sigma(I)$ were treated as unobserved, data reduction yielded respectively 920 and 2825 independent reflections for **5** and **6**.

Structure Solution and Refinement for 5 and 6. Both structures were solved by direct methods using SHELX.[9] Refinement was by full-matrix least squares with $\sum w\Delta^2$ being minimized. The S(CH$_3$)$_2$ group of **5** is statistically disordered about a crystallographic diad axis leading to overlap of the S(3) and C(3) electron densities in difference Fourier syntheses. This overlap is particularly severe for C(3) leading to observation of only one special position on the diad axis for this atom in the difference synthesis. (However, there was no evidence for any disorder in the S$_4$N$_4$ cradle.) For the refinement of C(3), the S(3)–C(3) bond was constrained to be equal to that of S(3)–C(4) with an allowed standard deviation of 0.005 Å. The final refined position of C(3) is 0.105 Å from the diad axis. The methyl groups were refined rigidly with d(C–H) = 1.08 Å and tetrahedral bond angles. A joint isotropic temperature factor assigned to the hydrogens refined to 0.051 (10) Å^2. The nonhydrogen atoms were refined anisotropically leading to terminal values of $R = 0.054$ and $R_w = 0.049$. The hydrogen atom positional parameters and their isotropic temperature factors were allowed to refine freely for **6**. Anisotropic refinement of the nonhydrogen atoms led to the terminal values $R = 0.036$ and $R_w = 0.039$. The weighting schemes for **5** and **6** were given by $w = k(\sigma^2(F_o) + 0.0002F_o^2)^{-1}$, where the scale factor k refined to 2.7930 and 1.0537, respectively. Scattering factors for the nonhydrogen atoms were taken from Cromer et al.[10] and for the hydrogen atoms from Stewart et al.[11] Computations were performed on a PDP 10 computer using SHELX (G. M. Sheldrick), ORTEP[12] (C. K. Johnson), and locally developed programs.

Results and Discussion

Pentasulfur hexanitride (**3**) may be prepared by reacting either Bu$_4$N$^+$S$_4$N$_5^-$ with bromine[3] or S$_3$N$_3$Cl$_3$ with N[Sn(CH$_3$)$_3$]$_3$ (**2**). It is not readily understandable why S$_5$N$_6$, a molecule with a basket-like structure, is formed. It is, however, possible to visualize its formation as occurring by the bridging of two of the four opposite sulfur atoms in S$_4$N$_4$ by an –N=S=N– group. In the reaction of Bu$_4$N$^+$S$_4$N$_5^-$ with bromine an appropriate intermediate could be S$_4$N$_4$Br$_2$ and in the reaction of S$_3$N$_3$Cl$_3$ the S$_4$N$_4$Cl$_2$ molecule, because in the second case we have isolated S$_4$N$_4$ as well as S$_4$N$_5$Cl as intermediates. It was, therefore, necessary to prepare S$_4$N$_4$Cl$_2$ (**1**) and react it with (CH$_3$)$_3$SiN=S=NSi(CH$_3$)$_3$ (**2**) in a molar ratio of 1:1. In fact, **3** is formed in high yield by this route. We extended this type of reaction in acetonitrile as solvent to (CH$_3$)$_3$SiN=S(CH$_3$)$_2$=NSi(CH$_3$)$_3$ (**4**) and obtained **5** as bright yellow transparent crystals.

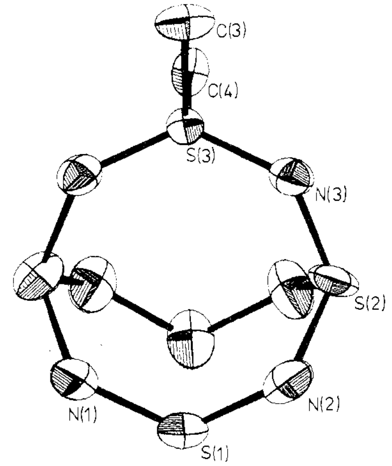
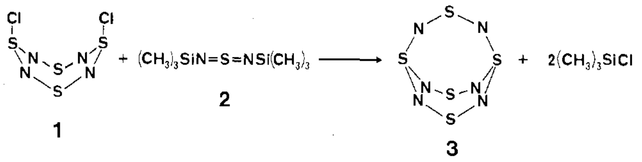
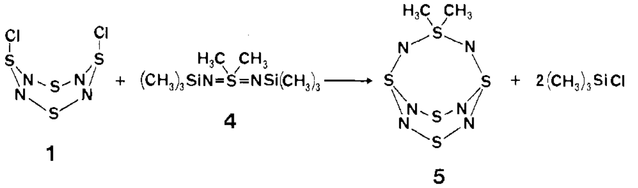


Figure 1. Perspective view of **5**. Thermal ellipsoids are shown at the 50% probability level. The positions of the hydrogen atoms have been omitted for the sake of clarity.





On the basis of mass spectral and analytical data and by comparison of the IR data of **5** with **3** we were able to assign a basket-like structure to **5**, which is confirmed by the X-ray structural analysis reported in this work. The comparison of the IR data of **5** with **3** indicates a shift of the absorptions in **5** to lower wavenumbers. The explosive nature of these compounds by heating or striking in the solid state is undoubtedly due to the high nitrogen content. **3** is a red and **5** a yellow crystalline solid.

The various reactions which were investigated for the formation of S$_5$N$_6$ are given in Scheme I. Small quantities of S$_5$N$_6$ and S$_4$N$_4$ were isolated from the reaction of S$_4$N$_4$Cl$_2$ with **4**. This suggests that dealkylation either of S$_5$N$_6$(CH$_3$)$_2$ or of **4** occurs. The identification of CH$_3$Cl in the system by mass spectra supports our argument on dealkylation. This result is in accordance with the reaction of S$_3$N$_3$Cl$_3$ and **4**, where

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[9] G. M. Sheldrick, "SHELX-76 Program for Crystal Structure Determination", Cambridge, England, 1976.

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[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[12] C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge Tenn., 1965.

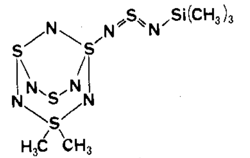
Table V. Atom Coordinates and Thermal Parameters (Å^2 × 10^3) for $S_5N_6(CH_3)_2$ (**5**) with Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	0.3555 (4)	0.2001 (3)	0.5497 (1)	79 (3)	44 (2)	46 (2)	−19 (2)	19 (2)	−16 (2)
S(1)	0.4489 (1)	0.2892 (1)	0.5255 (1)	68 (1)	65 (1)	38 (1)	−19 (1)	22 (1)	−20 (1)
N(2)	0.5490 (3)	0.3677 (4)	0.5506 (1)	44 (2)	81 (3)	44 (2)	−16 (2)	16 (2)	−11 (2)
S(2)	0.5113 (1)	0.4950 (1)	0.5753 (1)	44 (1)	45 (1)	32 (1)	5 (1)	0 (1)	−21 (1)
N(3)	0.4689 (3)	0.4607 (3)	0.6217 (1)	36 (2)	40 (2)	27 (1)	1 (1)	−1 (1)	−5 (1)
S(3)	0.3450 (1)	0.4069 (1)	0.6370 (1)	25 (1)	26 (1)	24 (1)	0 (1)	−1 (1)	1 (1)
C(3)	0.3657 (39)	0.3721 (30)	0.6886 (2)	33 (9)	52 (5)	21 (2)	−11 (10)	−3 (6)	−7 (5)
C(4)	0.2366 (6)	0.5303 (6)	0.6376 (2)	31 (4)	34 (4)	50 (4)	−5 (3)	−1 (3)	9 (3)

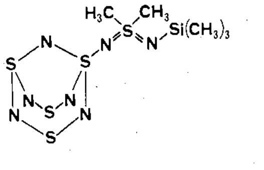
atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(1)[b]	0.2792	0.3404	0.7013	H(4)	0.1449	0.4977	0.6452
H(2)	0.3950	0.4563	0.7039	H(5)	0.2323	0.5874	0.6107
H(3)	0.4352	0.3005	0.6925	H(6)	0.2729	0.5849	0.6624

[a] The form of the anisotropic temperature factors is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$. [b] The hydrogen atoms were assigned a group isotropic temperature factor which refined to 0.051 (10) Å^2.

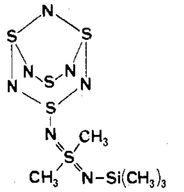
S_5N_6 and $S_5N_7Si(CH_3)_5$ (**6**) are formed in addition to the expected $[S_4N_5(CH_3)_2]^+Cl^-$. The formation of **6** can again be interpreted by a dealkylation step of **4** to yield **2** which is known to react with $S_3N_3Cl_3$ to yield S_4N_5Cl.[3] Indeed S_4N_5Cl could be isolated in minor amounts by the above reaction using CCl_4 as solvent.[6] The final step of the reaction may be explained by the reaction of S_4N_5Cl with **4** to yield **6**. It was independently demonstrated that these compounds react under formation of **6** in better yields. The composition of **6** was demonstrated on the basis of mass spectral and analytical data. Of the three logical structures compatible with the formulation $S_5N_7Si(CH_3)_5$, **6b** and **6c** are suggested by IR and ^{1}H NMR data. Only two signals at δ 3.5 (SCH_3) and δ 0.54 ($SiCH_3$) in the intensity ratio 2:3 are observed in the ^{1}H NMR spectrum. For **6a** two signals in the ratio 1:1 are to be expected for the SCH_3 groups as they are nonequivalent as was recently demonstrated for $[S_4N_5(CH_3)_2]^+SbCl_6^-$.[6] A distinction between **6b** and **6c** could only be given by X-ray analysis.



6a



6b



6c

The positional and thermal parameters of **5** are given in Table V, bond lengths and angles in comparison to S_5N_6 (**3**) are given in Table VI, and the molecular geometry is depicted in an ORTEP plot (Figure 1). The structure of **5** resembles that of a basket with an $-N{=}S(CH_3)_2{=}N-$ unit as the handle, which bridges two of the sulfur atoms of an S_4N_4 cradle. As may be seen from Table VI, the molecular dimensions of the cradle are similar to those of S_5N_6. The average N–S(1) bond distance of 1.602 Å in **5** is significantly shorter than that of 1.634 Å for the N–S(2) bond. The corresponding distances are 1.606 and 1.622 Å in **3**. An average S–N distance of 1.62 Å is observed for S_4N_4.[13] The transannular S···S separations are also similar for both **3** and **5**, with the S(1)···S(1)′ distance of 2.433 (3) Å 0.008 Å longer and the S(2)···S(2)′ distance of 3.908 (3) Å 0.03 Å shorter in the latter derivative. Values of 2.830 (3) and 2.829 (3) Å are observed for S(1)···S(2) and S(1)···S(2)′ in **5**.

Table VI. Bond Lengths (Å) and Angles (deg) in **3**[5] and **5**

	3	**5**
S(1)–N(1)	1.606 (3)	1.603 (4)
S(2)′–N(1)	1.623 (3)	1.628 (4)
N(2)–S(1)	1.606 (3)	1.601 (4)
S(1)–S(1)′	2.425 (2)	2.433 (3)
S(2)–N(2)	1.621 (3)	1.640 (4)
N(3)–S(2)	1.702 (3)	1.643 (3)
S(3)–N(3)	1.536 (3)	1.543 (3)
S(3)′–N(3)		1.523 (3)
S(3)–C(3)		1.760 (8)
S(3)–C(4)		1.765 (6)
S(2)′–N(1)–S(1)	121.7 (2)	122.2 (2)
N(1)–S(1)–N(2)	118.5 (2)	118.6 (2)
S(1)–N(2)–S(2)	120.6 (2)	121.7 (2)
N(2)–S(2)–N(1)′	105.7 (2)	103.5 (2)
N(3)–S(2)–N(1)′	109.2 (2)	110.4 (2)
N(3)–S(2)–N(2)	108.6 (2)	110.4 (2)
S(3)–N(3)–S(2)	137.1 (2)	129.2 (2)
N(3)–S(3)–N(3)′	126.3 (2)	126.4 (2)
C(3)–S(3)–N(3)		106.6 (14)
C(3)–S(3)–N(3)′		101.8 (14)
C(4)–S(3)–N(3)		107.5 (3)
C(4)–S(3)–N(3)′		108.7 (3)
C(3)–S(3)–C(4)		103.4 (11)

In contrast to the S_4N_4 cradle, the molecular dimensions of the $-N{=}S{=}N-$ handle show important changes on going from **3** to **5**. The N(3)–S(2) bond length of 1.643 (3) Å in **5** is similar to the N–S distances in the cradle and 0.059 Å shorter than that in **3**. At the same time the S(2)–N(3)–S(3) angle of 129.2 (2)° is 7.9° narrower in **5**. S_5N_6 displays twofold symmetry with S(3) occupying a special position on a crystallographic diad axis. Although S(3) in **5** is now tetracoordinated and displaced 0.47 Å from the diad axis, the average S(3)–N(3) distance of 1.533 Å and the N(3)–S(3)–N(3)′ bond angle of 126.4 (2)° are similar to the values of 1.536 (3) Å and 126.3 (2)° observed for **3**. Delocalization of the electrons in the $-N{=}S{=}N-$ handle is less favorable in **5** in comparison to **3** as a result of the increase in the coordination number of S(3) from 2 to 4. This leads to a displacement of S(3) from the plane of the other four handle atoms (i.e., including S(2) and S(2)′) and thereby to increased double bond character of the remaining N–S bond N(3)–S(2). As a result of the disorder of the $S(CH_3)_2$ group about the crystallographic diad axis, bond distances and angles involving C(3) are not of high reliability.

The positional and thermal parameters of **6** are given in Tables VII and VIII, bond lengths and angles are given in Tables IX and X, and the molecular geometry is given in Figure 2. It is instructive to compare the molecular dimensions of the neutral S_4N_5 system in **6** with those in the $S_4N_5^+$

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Table VII. Atom Coordinates and Thermal Parameters ($Å^2 \times 10^3$) for $S_5N_7Si(CH_3)_5$ (**6**) with Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	−0.3898 (1)	0.3703 (1)	0.7786 (1)	38 (1)	67 (1)	43 (1)	−12 (1)	8 (1)	−13 (1)
N(1)	−0.3399 (2)	0.4872 (3)	0.8432 (3)	44 (1)	62 (1)	44 (1)	3 (1)	13 (1)	−14 (1)
S(2)	−0.2929 (1)	0.5187 (1)	1.1014 (1)	42 (1)	32 (1)	50 (1)	−6 (1)	19 (1)	−8 (1)
N(2)	−0.1449 (2)	0.4445 (2)	1.1911 (3)	38 (1)	35 (1)	46 (1)	−9 (1)	16 (1)	−16 (1)
S(3)	−0.0838 (1)	0.2796 (1)	1.2359 (1)	29 (1)	38 (1)	30 (1)	−2 (1)	10 (1)	−10 (1)
N(3)	−0.1765 (2)	0.2115 (2)	1.2932 (3)	37 (1)	40 (1)	45 (1)	8 (1)	19 (1)	−9 (1)
S(4)	−0.3246 (1)	0.2849 (1)	1.2092 (1)	37 (1)	45 (1)	52 (1)	−3 (1)	22 (1)	−16 (1)
N(4)	−0.3764 (2)	0.2642 (3)	0.9475 (4)	46 (1)	51 (1)	65 (1)	−16 (1)	13 (1)	−19 (1)
N(5)	−0.3640 (2)	0.4480 (2)	1.2087 (3)	36 (1)	44 (1)	52 (1)	−9 (1)	23 (1)	−7 (1)
N(6)	−0.0778 (2)	0.2169 (2)	1.0156 (3)	32 (1)	35 (1)	35 (1)	−7 (1)	14 (1)	−15 (1)
S(6)	0.0226 (1)	0.2469 (1)	0.9360 (1)	27 (1)	28 (1)	28 (1)	−2 (1)	9 (1)	−10 (1)
C(1)	0.0513 (2)	0.1141 (3)	0.7795 (4)	48 (1)	38 (1)	41 (1)	−12 (1)	21 (1)	−17 (1)
C(2)	−0.0554 (2)	0.3932 (2)	0.7533 (3)	38 (1)	35 (1)	34 (1)	4 (1)	8 (1)	−13 (1)
N(7)	0.1373 (2)	0.2650 (2)	1.0863 (3)	29 (1)	35 (1)	38 (1)	−1 (1)	4 (1)	−13 (1)
Si	0.2682 (1)	0.1574 (1)	1.2749 (1)	30 (1)	35 (1)	40 (1)	3 (1)	5 (1)	−11 (1)
C(3)	0.2422 (3)	0.0050 (3)	1.3612 (5)	60 (2)	45 (2)	54 (2)	6 (1)	17 (1)	−19 (1)
C(4)	0.3954 (3)	0.1051 (4)	1.1641 (8)	44 (2)	71 (2)	120 (3)	27 (2)	41 (2)	2 (2)
C(5)	0.3052 (4)	0.2562 (4)	1.4980 (5)	91 (3)	59 (2)	49 (2)	0 (1)	−14 (2)	−31 (2)

[a] The form of the anisotropic temperature factors is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$.

Table VIII. Hydrogen Atom Positional Parameters and Isotropic Temperature Factors ($Å^2 \times 10^3$) for $S_5N_7Si(CH_3)_5$ with Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*	*U*
H(11)	0.0973 (25)	0.0286 (21)	0.8831 (37)	50 (8)
H(12)	−0.0315 (20)	0.1127 (32)	0.6720 (38)	61 (9)
H(13)	0.1215 (26)	0.1216 (36)	0.7214 (51)	72 (10)
H(21)	−0.1390 (21)	0.3843 (32)	0.6496 (40)	60 (9)
H(22)	0.0069 (23)	0.4117 (29)	0.6904 (42)	52 (8)
H(23)	−0.0827 (29)	0.4776 (22)	0.8262 (42)	58 (9)
H(31)	0.3324 (23)	−0.0589 (36)	1.4619 (54)	97 (13)
H(32)	0.1607 (27)	0.0237 (44)	1.4023 (66)	106 (14)
H(33)	0.2136 (46)	−0.0416 (45)	1.2222 (48)	126 (17)
H(41)	0.4811 (32)	0.0311 (46)	1.2497 (80)	155 (21)
H(42)	0.3850 (59)	0.0291 (46)	1.0689 (77)	159 (25)
H(43)	0.4194 (54)	0.1747 (47)	1.0867 (80)	159 (22)
H(51)	0.3773 (32)	0.1867 (38)	1.6194 (54)	117 (16)
H(52)	0.2290 (34)	0.2985 (52)	1.5511 (75)	136 (20)
H(53)	0.3202 (36)	0.3395 (29)	1.4450 (56)	87 (12)

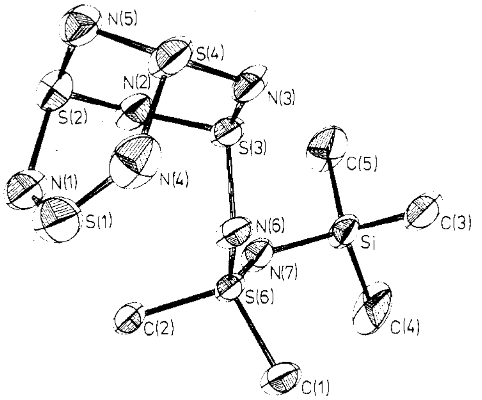

Figure 2. Perspective view of **6**. Thermal ellipsoids are shown at the 50% probability level. The positions of the hydrogen atoms have been omitted for the sake of clarity.

Table IX. Bond Distances (Å) and Angles (deg) in **6** and Other S_4N_5 Derivatives

	6	$S_4N_5^+$	$S_4N_5^-$	$S_4N_5O^-$
S(1)–N(1)	1.533 (3)	1.545 (4)	1.61 (2)	1.603 (3)
N(1)–S(2)	1.731 (2)	1.674 (4)	1.63 (3)	1.651 (4)
S(2)–N(2)	1.602 (2)	1.674 (4)	1.65 (2)	1.651 (4)
N(2)–S(3)	1.636 (2)	1.545 (4)	1.57 (2)	1.603 (3)
S(3)–N(3)	1.641 (3)	1.558 (4)	1.60 (2)	1.631 (4)
N(3)–S(4)	1.603 (2)	1.689 (4)	1.65 (2)	1.591 (3)
S(4)–N(4)	1.726 (3)	1.689 (4)	1.62 (2)	1.591 (3)
N(4)–S(1)	1.537 (3)	1.558 (4)	1.63 (2)	1.631 (4)
S(2)–N(5)	1.620 (3)	1.638 (5)	1.68 (2)	1.658 (4)
S(4)–N(5)	1.624 (2)	1.620 (5)	1.64 (2)	1.580 (4)
S(1)···S(2)	2.846 (1)	2.813 (2)	2.72 (1)	2.741 (1)
S(2)···S(3)	2.825 (1)	2.813 (2)	2.73 (1)	2.741 (1)
S(3)···S(4)	2.825 (1)	2.811 (1)	2.72 (1)	2.658 (1)
S(4)···S(1)	2.846 (1)	2.811 (1)	2.71 (1)	2.658 (1)
S(1)···S(3)	3.814 (1)	4.01	2.71 (1)	2.633 (1)
S(2)···S(4)	2.736 (1)	2.777 (2)	2.75 (1)	2.717 (2)
N(4)–S(1)–N(1)	119.5 (1)	119.5 (2)	114 (1)	111.7 (2)
S(1)–N(1)–S(2)	121.2 (2)	121.7 (2)	114 (1)	114.8 (2)
N(1)–S(2)–N(2)	105.7 (1)		100 (1)	98.8 (2)
S(2)–N(2)–S(3)	121.4 (2)	121.7 (2)	115 (1)	114.8 (2)
N(2)–S(3)–N(3)	111.9 (1)	119.5 (2)	114 (1)	111.7 (2)
S(3)–N(3)–S(4)	121.1 (1)	119.9 (2)	114 (1)	111.2 (2)
N(3)–S(4)–N(4)	106.7 (1)		101 (1)	105.0 (2)
S(4)–N(4)–S(1)	121.3 (2)	119.9 (2)	113 (1)	111.2 (2)
N(1)–S(2)–N(5)	104.2 (1)	107.1 (2)	110 (1)	107.5 (2)
N(2)–S(2)–N(5)	111.5 (1)	107.1 (2)	109 (1)	107.5 (2)
N(3)–S(4)–N(5)	112.5 (1)	108.7 (2)	111 (1)	111.2 (1)
N(4)–S(4)–N(5)	103.3 (1)	108.7 (2)	110 (1)	111.2 (1)
S(2)–N(5)–S(4)	115.0 (1)	117.0 (3)	112 (1)	114.1 (3)

Table X. Additional Bond Distances (Å) and Bond Angles (deg) in **6**

S(3)–N(6)	1.651 (2)	S(6)–C(2)	1.768 (2)
N(6)–S(6)	1.587 (2)	Si–C(3)	1.854 (4)
S(6)–N(7)	1.497 (2)	Si–C(4)	1.849 (5)
N(7)–Si	1.725 (2)	Si–C(5)	1.852 (4)
S(6)–C(1)	1.767 (3)		

N(2)–S(3)–N(6)	109.1 (1)	N(7)–S(6)–C(2)	107.6 (1)
N(3)–S(3)–N(6)	101.3 (1)	C(1)–S(6)–C(2)	103.7 (1)
S(3)–N(6)–S(6)	113.5 (1)	N(7)–Si–C(3)	112.4 (1)
N(6)–S(6)–N(7)	121.0 (1)	N(7)–Si–C(4)	108.0 (2)
S(6)–N(7)–Si	133.7 (1)	N(7)–Si–C(5)	106.1 (1)
N(6)–S(6)–C(1)	100.9 (1)	C(3)–Si–C(4)	109.3 (2)
N(7)–S(6)–C(1)	114.7 (1)	C(3)–Si–C(5)	109.7 (2)
N(6)–S(6)–C(2)	107.4 (1)	C(3)–Si–C(6)	111.3 (2)

cation,[3] the $S_4N_5^-$ anion,[4] and the $S_4N_5O^-$ anion[2] (Table IX). Chlorine ions symmetrically bridge S_4N_5 units via S(1) and S(3) in the $S_4N_5^+$ cation. In $S_4N_5O^-$ the exocyclic oxygen is connected to S(4), which is bonded to three nitrogen atoms. Both the $S_4N_5^+$ cation and the $S_4N_5O^-$ anion are bisected by crystallographic mirror planes through S(2), N(5), and S(4). The molecular dimensions of the $S_4N_5^-$ anion are in accordance with an approximate mirror plane through these atoms. Obviously such a symmetry is not possible in **6**. The neutral S_4N_5 unit displays, however, an approximate plane of symmetry through S(1), N(5), and N(3) as also observed in $S_4N_5^+$ and $S_4N_5^-$. The bond lengths in the six-membered S_3N_3 ring containing S(2), S(3), and S(4) lie within the range 1.602–1.641 Å comparable with the average value of 1.62 Å in S_4N_4.[12] In contrast, the S(2)–N(1) and S(4)–N(4) bonds with distances of 1.731 (2) and 1.726 (3) Å display predom-

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inately single-bond character and the S(1)–N(1) and S(1)–N(4) bonds with distances of 1.533 (3) and 1.537 (3) Å double bond character. These distances are similar to those of 1.702 (3) and 1.536 (3) Å for the formally single and double S–N bonds in the –N=S=N– handle of S_5N_6.[5] Perhaps the best way of regarding the structure of the S_4N_5 unit in **6** is, therefore, as an S_3N_3 ring with a high degree of π delocalization bridged by an –N=S=N– unit between S(2) and S(4). This description is not surprising as the three sulfur atoms in the S_3N_3 ring all display the coordination number 3, that in the –N=S=N– handle displays only 2. Raising the coordination number of sulfur leads to a contraction of its orbitals allowing thereby a better overlap with nitrogen orbitals, which leads to an increase in S–N bond strength. The S_3N_3 ring containing S(2), S(3), and S(4) is in a chair conformation with S(3) and N(5) displaced –0.365 and 0.616 Å from the least-squares plane through the remaining four atoms (distances: N(3), –0.009; S(4), 0.009; S(2), –0.009; N(2), 0.009 Å). In contrast the second S_3N_3 ring containing S(1), S(2), and S(4) displays a basically envelope conformation with N(5) as the flap. The distances from the least-squares plane through N(1), S(2), S(4), and N(4) are as follows: S(1), –0.112; N(1), 0.017; S(2), –0.017; N(5), –0.765; S(4), 0.017; N(4), –0.017 Å. Whereas the anions $S_4N_5^-$ and $S_4N_5O^-$ display six S···S separations of length respectively 2.71–2.75 and 2.63–2.74 Å, only five such interactions in the range 2.78–2.81 Å are to be observed for $S_4N_5^+$. The sixth pair of sulfur atoms S(1) and S(3) are at 4.01 Å from another. A similar state of affairs is observed in **6** where five S···S interactions are found in the range 2.736–2.846 Å with the sixth distance S(1)···S(3) = 3.814 (1) Å. This distance is presumably longer in $S_4N_5^+$ as a result of some preferential delocalization of cation charge on the sulfur atoms S(1) and S(3) in this moiety.[3]

The striking difference in the N–S distances to S(6) in the side chain of **6** correlates with the observation that the bond angle at N(7) is 20.2° wider than at N(5). Similar short N–S distances of 1.507 and 1.498 Å have been observed for this bond in the derivatives $(CH_3)_2Si_2N_6S_3$[14] and $(CH_3)_4Si_2N_4S_2$[15] when the nitrogen is at the same time bonded to silicon. This may be caused by a change in the electron density of the σ skeleton, an effect which is known for silicon.[16] The N–Si distance of 1.725 (2) Å lies in typical range for this bond.[17]

Acknowledgment. The authors are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work. M.N.S.R. thanks the Alexander von Humboldt-Foundation for the award of a fellowship.

Registry No. **1**, 71699-97-3; **2**, 18156-25-7; **3**, 68993-02-2; **4**, 19923-46-7; **5**, 71901-54-7; **6**, 71901-55-8; $N[Sn(CH_3)_3]_3$, 1068-70-8.

Supplementary Material Available: Compilations of observed and calculated structure factors on an absolute scale (22 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Magnetic Properties of the Cluster Complex $Cu^I_8Cu^{II}_6[SC(CH_3)_2CH_2NH_2]_{12}Cl\cdot 3.5SO_4\cdot{\sim}20H_2O$, a Mixed-Valence Copper–Mercaptide Species

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Received June 7, 1979

The structure of the title complex (**1**) has been determined from three-dimensional X-ray data. $Cu^I_8Cu^{II}_6[SC(CH_3)_2CH_2NH_2]_{12}Cl\cdot 3.5SO_4\cdot{\sim}20H_2O$ crystallizes in space group $C2/c$ (C_{2h}^6, No. 15) with $Z = 4$, $a = 18.318$ (3) Å, $b = 21.826$ (5) Å, $c = 28.829$ (6) Å, $\beta = 110.17$ (1)°, $d_{calcd} = 1.763$, and $d_{obsd} = 1.79$ (1) g/cm³. Least-squares refinement of 4790 reflections having $F^2 > 3\sigma(F^2)$ gave a conventional R factor of 0.10. The structure consists of discrete, centrosymmetric $Cu^I_8Cu^{II}_6[SC(CH_3)_2CH_2NH_2]_{12}Cl^{7+}$ clusters in which 14 copper ions are linked by 12 three-coordinate mercaptide ions and an eight-coordinate chloride ion. Each cluster contains a $Cu_{14}S_{12}Cl$ core similar to that reported for a related, anionic $Cu_{14}[SC(CH_3)_2CH(CO_2)NH_2]_{12}Cl^{5-}$ complex. The core consists of a distorted icosahedral arrangement of 12 sulfur atoms with 8 of the 20 triangular icosahedral faces occupied by cuprous ions which form an approximate cube (Cu(I)···Cu(I) = 3.264 (4)–3.341 (3) Å). The chloride ion is located at the common center of the cube and icosahedron. The remaining six core copper ions are cupric species which are located approximately along 6 of the 30 icosahedral edges to form a distorted octahedral array (Cu(II)···Cu(II) = 6.645 (4)–6.825 (4) Å). All core copper species are four-coordinate. The cupric species have approximately planar cis S_2N_2 ligand sets while the cuprous species show dominant triangular planar coordination geometry arising from S_3 ligation (Cu(I)–S = 2.268 (5)–2.297 (5) Å) with weakly bound apical chloride ions (Cu(I)–Cl = 2.852 (3)–2.880 (3) Å) oriented approximately normal to each triangular planar CuS_3 unit. Electronic spectral and magnetic properties of the title complex are presented and discussed. Effective magnetic moments of **1** fell in the range 1.79–2.50 μ_B at temperatures between 286 and 7.9 K; below 7.9 K, the magnetic moment decreased steadily to 2.37 μ_B at 4.2 K. Computer fits of the susceptibility data using the $\hat{H} = -2J\hat{S}_1\hat{S}_2$ spin–spin coupling model with $g = 2.066$ gave J values in the range 4.9–5.2 cm⁻¹. It is suggested that the observed ferromagnetic exchange interaction between Cu(II) ions is transmitted via S–Cu(I)–S superexchange pathways within the cluster. At both X- and Q-band frequencies and temperatures ranging from 300 to 9 K, EPR powder spectra of **1** consisted of a single derivative signal which we interpret as arising from electron exchange between Cu(II) ions at a frequency exceeding the difference between $g_\parallel$ and $g_\perp$ values. From an analysis of the electronic spectra of **1**, the intense purple color is attributed to σ(S) → Cu(II) charge transfer (ϵ ~3400 per Cu(II)). Structural, magnetic, and electronic spectral data suggest that the cluster contains discrete Cu(I) and Cu(II) ions. We suggest that the Cu(II) ions in effect are ligated by the $Cu^I_8S_{12}Cl^{5-}$ substructure and its 12 aminoethyl "tails". Lastly, the synthesis and partial characterization of two yellow complexes which are oxidized by air to form **1** are described.

Introduction

Chemical studies of the copper–D-penicillamine (HSC-$(CH_3)_2CHNH_3^+CO_2^-$) system may help illuminate the mechanism by which this drug mobilizes and promotes the urinary excretion of excess copper associated with Wilson's and other chronic liver diseases.[2] Patients undergoing oral

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0020-1669/80/1319-0543$01.00/0